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CONCEPT MAP

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BRAINSTORMING PROBLEMS

Physical Chemistry



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The system of Ayurveda is as old as the ancient history of India. Luckily for us, in spite of repeated invasions, we had retained the purity of our ancient knowledge.

We are also absorbing modern systems of knowledge followed by research of the highest order, at par with any nation.

However in the these days, we have also to learn to make money like the developed countries.

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Anil Ahlawat
Editor

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ASSERTION & REASON

AIIMS Special

Directions : Mark the correct choice as:

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- (d) If both assertion and reason are false.

PHYSICAL CHEMISTRY

1. **Assertion :** The volume of a gas is directly proportional to the number of moles of the gas.

Reason : The ratio of the volumes of the reactants to products are in agreement with their molar ratio.

2. **Assertion :** The decomposition of NH_3 on finely divided platinum surface is first order when the concentration is low, however at higher concentration, the reaction becomes zero order.

Reason : In first order reaction, the rate of reaction is proportional to the first power of the concentration of the reactant.

3. **Assertion :** In the reaction,
$$\text{SO}_2\text{Cl}_{2(g)} \rightleftharpoons \text{SO}_{2(g)} + \text{Cl}_{2(g)}$$
the reaction shifts to backward direction on increasing pressure.

Reason : The increase in pressure at equilibrium shifts the reaction towards lesser number of moles.

4. **Assertion :** Zinc blende and wurtzite both have fcc arrangement of sulphide ions.

Reason : There are four formula units of ZnS in both.

5. **Assertion :** Enthalpy changes are positive when $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and salt like NaCl , KCl etc. (which do not form hydrates) are dissolved in water. But enthalpy changes are

negative when anhydrous salts capable of forming hydrates are dissolved in water.

Reason : The difference in the behaviour is due to large difference in the molecular weights of hydrated and anhydrous salts. The substance with larger molecular weight usually shows positive enthalpy changes on dissolution.

6. **Assertion :** SeCl_4 does not have a tetrahedral structure.

Reason : Se in SeCl_4 has two lone pairs of electron.

7. **Assertion :** Equivalent weight of KMnO_4 in acidic medium is $M/5$ (M = mol. wt.) while in basic medium, it is equal to $M/3$.

Reason : In acidic medium, 1 mol of MnO_4^- gains 5 electrons while in basic medium it gains 3 electrons.

8. **Assertion :** Galvanic cells containing hydrogen, methane, methanol etc. as fuels are called fuel cells.

Reason : They are designed to convert the energy of combustion of fuels directly into electrical energy.

9. **Assertion :** BF_3 is a weaker Lewis acid than BCl_3 .

Reason : The planar BF_3 molecule is stabilized to a greater extent than BCl_3 by B - X π -bonding.

10. Assertion : In Sommerfeld model, circular orbit is possible for the electron in K-shell.

Reason : Electron present in K-shell corresponds to principal quantum number $n = 1$.

ORGANIC CHEMISTRY

11. Assertion : Cyclohexanone exhibits keto-enol tautomerism.

Reason : In cyclohexanone, one form contains the keto group ($C=O$) while other contains enolic group ($-C=C-OH$).

12. Assertion : Oxiranes are cleaved under acidic and basic conditions.

Reason : The oxirane ring is strained and the tetrahedral bond angle (109.5°) is distorted to 61.5° .

13. Assertion : Greater the stability of carbanion, greater is its ease of formation and hence, more reactive is the aryl halide.

Reason : Chlorobenzene is less reactive than *p*-chloroanisole towards nucleophilic substitution reactions.

14. Assertion : Ethanal on treatment with selenium dioxide can be converted directly into glyoxal.

Reason : SeO_2 oxidizes the methylene group adjacent to $C=O$ group in aldehydes or ketones to carbonyl group.

15. Assertion : *m*-Chlorobenzoic acid is a stronger acid than *p*-chlorobenzoic acid.

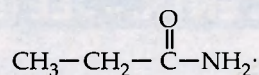
Reason : In *m*-chlorobenzoic acid both $-I$ -effect and $+R$ -effect of Cl operate but in *p*-chlorobenzoic acid only $+R$ -effect of Cl operates.

16. Assertion : [10]-Annulene is not aromatic though it contains Huckel number of π -electrons.

Reason : Steric interaction between internal hydrogens makes it non-planar.

17. Assertion : $(CH_3)_2CH-\overset{\overset{O}{\parallel}}{C}-NH_2$ undergoes faster Hofmann-bromamide

reaction in comparison to



Reason : $(CH_3)_2CH-$ migrates faster than CH_3-CH_2- at electron-deficient nitrogen atom.

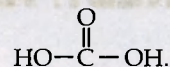
18. Assertion : Me_3N reacts with BF_3 whereas Ph_3N does not.

Reason : The electron pair on nitrogen atom in Ph_3N is delocalised in the benzene ring and is not available to boron in BF_3 .

19. Assertion : Fructose does not contain an aldehyde group but still reduces Tollen's reagent.

Reason : In presence of a base, fructose undergoes rearrangement to form a molecule containing an aldehyde group.

20. Assertion : $H-\overset{\overset{O}{\parallel}}{C}-OH$ is less acidic than



Reason : $-H$ is electron releasing while $-OH$ is electron withdrawing group.

INORGANIC CHEMISTRY

21. Assertion : Nitrogen is unreactive at room temperature but becomes reactive at elevated temperatures (on heating) or in the presence of catalyst.

Reason : In nitrogen molecules, there is extensive delocalization of electrons.

22. Assertion : F-atom has less negative electron affinity than Cl-atom.

Reason : Additional electrons are repelled more effectively by $3p$ -electrons in Cl-atom than by $2p$ -electrons in F-atom.

23. Assertion : Al is obtained by high temperature reduction of alumina with carbon.

Reason : Alumina reacts with carbon to form aluminium carbide which decomposes at high temperature to

form Al, while carbon is oxidized to CO.

24. Assertion : The degree of complex formation in actinides decreases in the order $M^{4+} > MO_2^{2+} > M^{3+} > MO_2$.

Reason : Actinides form complexes with π -bonding ligands such as alkyl phosphines and thioethers.

25. Assertion : In water, orthoboric acid behaves as a weak monobasic acid.

Reason : In water, orthoboric acid acts as a proton donor.

26. Assertion : Ozone is a more powerful oxidizing agent than O_2 .

Reason : Ozone is diamagnetic but O_2 is paramagnetic.

27. Assertion : $[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless.

Reason : $d-d$ transition is not possible in $[Sc(H_2O)_6]^{3+}$.

28. Assertion : Lanthanoids show a limited number of oxidation states whereas actinoids show a large number of oxidation states.

Reason : Energy gap between $4f$, $5d$ and $6s$ -subshells is large, whereas that between $5f$, $6d$ and $7s$ -subshells is small.

29. Assertion : In fused state, calcium chloride cannot be used to dry alcohol or NH_3 .

Reason : $CaCl_2$ is not a good desiccant.

30. Assertion : Wolframite impurities are separated from cassiterite by electromagnetic separation.

Reason : Cassiterite being magnetic is attracted by the magnet and forms a separate heap.

SOLUTIONS

1. (b): $V = \frac{nRT}{P}$, i.e., $V \propto n$. Volumes of gases are in the ratio of their moles.

2. (b): In a heterogeneous system, the reactant is absorbed on the surface of a solid catalyst. The fraction of the surface of the catalyst covered by the reactant is proportional to its concentration at low values and the rate of reaction is first order.

However at higher concentration, the surface of the catalyst is fully adsorbed, so any amount of ammonia added does not change the adsorption process so the reaction rate becomes independent of the concentration and it becomes zero order reaction.

3. (a): As the pressure of the gaseous system is increased the volume occupied by the system decreases so that total number of moles per unit volume increases. To undo this stress, the reaction proceeds towards lesser number of moles of gaseous substances so that the increased pressure is reduced. This is in accordance to Le Chatelier's principle.

4. (d) : Wurtzite is built from two interpenetrating *hcp* lattices as opposed to the *fcc* lattices in zinc blende. Wurtzite has two ZnS while zinc blende has four ZnS in unit cell.

5. (c) : The exothermic or endothermic behaviour of dissolution depends only upon the nature of the salt and not on its molecular weight.

6. (c) : $SeCl_4$ has distorted trigonal bipyramidal structure. Se in $SeCl_4$ has one lone pair of electron.

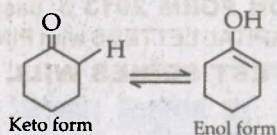
7. (a): $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ (In acidic medium)
 $MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$ (In basic medium)

8. (a)

9. (a) : There is greater $p\pi - p\pi$ back bonding in BF_3 .

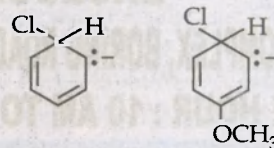
10. (b): Sommerfeld model is an extension of Bohr's model. Electrons in an atom revolve around the nuclei in elliptical orbit. The circular path is a special case of elliptical orbit.

11. (a) : In cyclohexanone, keto-enol tautomerism is as follows.



12. (b)

13. (c) : On comparing the relative stabilities of carbanion of chlorobenzene and *p*-chloroanisole,

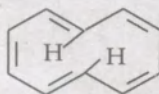


The electron donating group ($-\text{OCH}_3$) in anisole tends to intensify the negative charge relative to carbanion in chlorobenzene. Thus, *p*-chloroanisole is less reactive than chlorobenzene.

14. (a)

15. (c): *m*-chlorobenzoic show only $-I$ effect but *p*-chlorobenzoic acid show both $-I$ and $+R$ effects, hence *m*-chlorobenzoic acid is a stronger acid.

16. (a): Due to severe non-bonded interactions between the internal hydrogens (as shown in figure), the ring assumes non-planar geometry.



17. (a)

18. (a)

19. (a): Under basic conditions, the fructose molecules have the location of the carbonyl bond switched to convert them into a glucose molecule.

20. (d): Peroxycarboxylic acids are about 1000 times weaker than the parent carboxylic acid, owing to the absence of resonance stabilization of the anion.

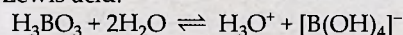
21. (c): At elevated temperature or in the presence of catalyst, strong bonds between two N-atoms rupture and makes N_2 molecule reactive.

22. (c): Additional electrons are repelled more effectively by $2p$ -electrons in F-atom than by $3p$ -electrons in Cl-atom.

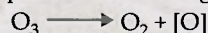
23. (c)

24. (b): Higher the charge on the metal ion, smaller is the ionic size and more is the complex forming ability. Thus, the degree of complex formation decreases in the order $M^{4+} > \text{MO}_2^{2+} > M^{3+} > \text{MO}_2^+$. The higher tendency of complex formation of MO_2^{2+} as compared to M^{3+} is due to high concentration of charge on metal atom M in MO_2^+ .

25. (c): Orthoboric acid (H_3BO_3) is soluble in water and behaves as a monobasic acid. It does not donate protons. Hence, it is not a protic acid but is a Lewis acid.



26. (b): Ozone can liberate nascent oxygen, so it acts as a powerful oxidizing agent.



27. (a): $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ has no unpaired electron in its d -subshell and thus $d-d$ transition is not possible whereas $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ has one unpaired electron in its d -subshell which gives rise to $d-d$ transition to impart colour.

28. (a)

29. (c): CaCl_2 forms addition products with alcohol and ammonia.

30. (c): Wolframite (FeWO_4) being magnetic is attracted by the magnetic roller and forms a heap under it.

OO

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Scrapbook

Mukul C. Ray, Odisha

Inorganic Chemistry always provides breathing space in IIT entrance examination as these questions take very little time to answer. Also there is hardly any chance (except a few chapters) where we see twists and turns in questions. So it is more important for you to go through proper texts rather than practicing the questions. These few pages will give you a vivid revision of general discussion on metals. No need to remember the data such as melting points, radii etc. Just remember the trend. They are incorporated for your convenience.

GROUP-1A

Members : Li, Na, K, Rb, Cs

□ **General Properties**

○ **Size**

	Li	Na	K	Rb
van der Waals radii (in pm)	180	231	231	244
Metallic radii (in pm)	157	191	235	250
Covalent radii (in pm)	123	154	203	216
Ionic radii (M^+) (in pm)	60	95	133	148

Note : K^+ (133 pm), Cu^+ (96 pm) Ag^+ (126 pm)

○ Melting points, boiling points and heat of atomisation all decreases gradually from top to bottom.

Density : Li Na K Rb Cs
(g/mL at 20°C) 0.534 0.968 0.86 1.53 1.87

Note : K has lower density than Na, also Li, Na, K have density values less than the density of water. Li is the lightest among all metals known.

○ Relative hydrated ionic radii decreases in the order : $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ and conducting power of ions in aq. solution.

$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$

○ Standard oxidation potential :

 Li Na K Rb Cs
 E°_{OP} (in volts) 3.05 2.71 2.93 2.93 2.99

Note : Li is the strongest reducing agent in aqueous solution.

○ Hydrated salts : Except Li salts, they crystallise from aqueous solutions in the anhydrous state. (Explanation : The hydration energy is not sufficient to overcome the loss in lattice energy due to inclusion of the larger hydrated ion). Li^+ forms trihydrate : $LiX \cdot 3H_2O$, $X = Cl^-, Br^-, I^-, ClO_3^-, ClO_4^-, MnO_4^-, NO_3^-$.

Notes : Li^+ does not form alums probably because the small $Li(H_2O)_6$ is too small to form a stable lattice required for alum formation.

→ $NaBiO_3$ perchlorates of K, Rb and Cs are water insoluble.

○ Complexing ability : It decreases from $Li > Na > K$.

□ **Abnormal behaviour of Lithium**

○ It is immiscible with molten K, Rb and Cs but miscible with Na only above 380°C.

○ Li_2CO_3 and $LiNO_3$ decompose readily on heating to oxides like Mg salts.

○ Li on heating with N_2 forms Li_3N ; others fail.

○ Many simple lithium salts are normally hydrated and the anhydrous salts are extremely hygroscopic (e.g. $LiCl$, $LiBr$).

Note : As regards nitrides, very high lattice energy is required to overcome the high bond energy of nitrogen plus its negative electron affinity. This seems to be attained only in Li_3N .

○ Reactivity decreases from Li to Cs. If you see it carefully it is exclusively because of kinetic factors. Because Li products are thermodynamically more stable owing to high lattice energy and hydration energy.

□ Extraction

- Lithium is usually extracted from spodumene [$\text{LiAl}(\text{SiO}_3)_2$]. It is converted into LiCl and Li is extracted from fused mixture containing 55% LiCl + 45% KCl at 450°C .
- Sodium is extracted by electrolysis of fused CaCl_2 (65%) and NaCl mixture at 505°C .
- Potassium is isolated by reducing molten KCl in a packed fractionating tower by rising Na -vapour.
 $\text{KCl} + \text{Na} \rightarrow \text{NaCl} + \text{K}$

Though this is contrary to our expectation from the reactivity trend ($\text{K} > \text{Na}$). But this has been possible because of high volatility of K in the temperature range $850\text{--}880^\circ\text{C}$.

Note : Electrolysis of fused KCl alone is also difficult as its melting point is 790°C and boiling point of potassium metal is 760°C . Attempts to lower the melting point by adding other metal salts have also failed. Because K^+ ions have a higher discharge potential than the metal added and potassium is very soluble in molten potassium chloride.

□ Uses

- Li metal is used as scavenger in metallurgy to remove O_2 and N_2 gases. Li is a good alloying metal and forms high strength, low density aluminium alloys for aircraft construction.
- Na metal is used as a reducing agent in the extraction of Ti , Zr etc. Na-K alloy is the most favoured material for heat exchange in fast breeder nuclear reactor.

Note : A breeder reactor is a nuclear reactor capable of generating more fissile material than it consumes. It produces fissile material from Th^{232} and U^{238} .

□ General Chemical Behaviour

- Oxides, Superoxides and Peroxides

When burnt in air, Li forms Li_2O , Na gives Na_2O_2 and K , Rb , Cs form superoxides.

Li_2O	Na_2O	K_2O	Rb_2O	Cs_2O
White	White	Gold white	Pale yellow	Orange

These colours are most probably due to lattice defects.

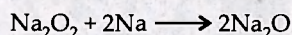
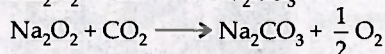
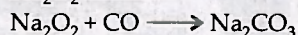
Li_2O_2	Na_2O_2	K_2O_2	Rb_2O_2	Cs_2O_2
White	Pale yellow	Orange	Dark brown	Yellow

Colours are due to defective lattice and small amounts of superoxides.

The peroxides contain peroxide ion, O_2^{2-} and thus liberate H_2O_2 with water or dilute acids.



Na_2O_2 reacts as :

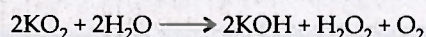


Notes : Solid dry hydroxides of Na , K , Rb and Cs interact with O_3 to form MO_3 (orange colour).

NaO_2	KO_2	RbO_2	CsO_2
Yellow	Orange	Dark brown	Orange

Superoxide ion has one unpaired e^- ; that is why superoxides are coloured and paramagnetic.

Crystals of Li_2O , Na_2O , K_2O , Rb_2O have antifluorite structure. Superoxides react vigorously with water.

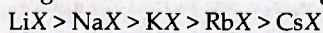


Their (KO_2 , RbO_2 , CsO_2) thermal decomposition give sesquioxides with formula M_2O_3 . Solubility of superoxides and oxides increases as the metal ions increases. The alkali metal hydroxides are all very strong bases. Boiling point decreases gradually. Vapour mostly consists of dimers. In the gas phase, basic strength increases. In aqueous solutions; they appear nearly equally strong due to levelling effect of the solvent.

NaOH is mostly produced by the electrolysis of brine solution using graphite anode and mercury cathode (brine solution is NaCl solution with concentration ranging from 3.5% to 26%).

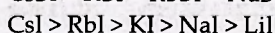
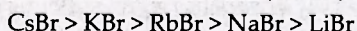
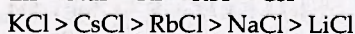
- Halides :

Negative value of lattice energy :



($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$)

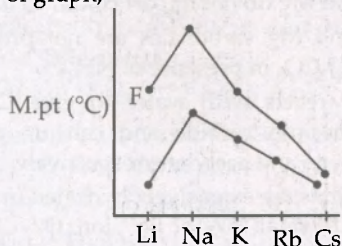
Negative value of enthalpy of formation :



Melting points of halides ($^\circ\text{C}$) :

	F^-	Cl^-	Br^-	I^-
Li	845	610	547	446
Na	995	808	755	661
K	856	772	748	677
Rb	775	717	682	642
Cs	682	645	636	621

In terms of graph,



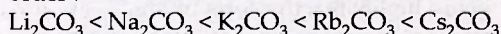
Notes: Due to small size of F⁻ ion, the lattice energy term predominates. This leads to a decreasing trend in the enthalpy of formation from LiF to CsF. For the large halides, lattice energy becomes less dominant.

→ Li salts have very low melting points because Li⁺ ions are quite small in size that results anion-anion repulsion. The actual Li - X distance is larger than expected. For fluorides, solubility increases greatly from LiF to CsF. (lattice energy decreases more rapidly). For iodides, solubility decreases (hydration energy decreases more rapidly) as NaI > LiI > RbI > KI > CsI. For chlorides and bromides, the solubility order is: LiX > CsX > RbX > NaX > KX (X = Cl⁻, Br⁻).

→ All the halides except CsCl, CsBr and CsI, adopt NaCl type structure.

Carbonates, bicarbonates:

Thermal stability of carbonates change in the order:



Li₂CO₃ is water insoluble. From Na₂CO₃ onwards, solubility increases.

Notes: High thermal instability of Li₂CO₃ is attributed to two major factors; Li⁺ ion exerts strong polarising action on CO₃²⁻ ion and high lattice energy of Li₂O than Li₂CO₃.

→ Except Li, all other alkali metals form solid bicarbonates. LiHCO₃ is known only in solution. Stability increases from LiHCO₃ to CsHCO₃.

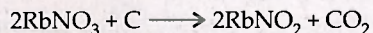
→ Solubility of bicarbonates increases from Li to Cs. Bicarbonates are less soluble than carbonates.

→ NaHCO₃ has an infinite chain of unsymmetrical H-bonds. KHCO₃ is dimeric. Lower solubility of NaHCO₃ is probably due to its H-bonded structure.

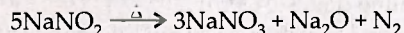
Nitrates and Sulphates:

Except LiNO₃, other alkali metal nitrates decompose on heating, giving off oxygen. LiNO₃ decomposes directly to the oxide. Thermal stability of nitrates increases with increasing atomic number.

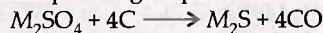
Nitrites may be prepared by heating nitrates with 'C'.



Nitrites disproportionate on heating in absence of air.



All the sulphates (except Li₂SO₄) are water soluble. On fusion with carbon, they are reduced to corresponding sulphides.



Note: LiCl and LiNO₃ are soluble in alcohol. LiCl is deliquescent while NaCl, KBr are not.

Hydrides:

Stability order of hydrides decreases in the order: LiH > NaH > KH > RbH > CsH

This is because of lowering of lattice energy down the group.

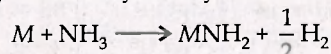
Solutions in NH_{3(l)}:

Alkali metals dissolve in NH_{3(l)} without evolution of H₂. The solubility increases from Li to Na to K. The solutions are blue when dilute but become bronze coloured at higher concentration.

They are good conductors; conductivity decreases as the solution becomes more and more concentrated and then again increases sharply after 0.05 M concentration. Saturated solution practically conduct electricity like liquid metals.

The dilute solutions are paramagnetic. The paramagnetic susceptibility decreases with increasing concentration. Around the region of minimum conductivity, the solution becomes diamagnetic. At still higher concentrations, the solution again become weakly paramagnetic.

The solutions of alkali metals in liq. NH₃ are not very stable; they readily form amides.



But in absence of catalytic impurities and under strictly anhydrous condition, such solutions are fairly stable.

Note: At high concentration M_{am}⁺ and e_{am}⁻ exist as (M_{am})₂ (e_{am})₂, a dimer that lowers conductivity and paramagnetism. At very high concentration, there are no liq. NH₃ molecules to solvate e⁻.

GROUP-II A

Members: Be, Mg, Ca, Sr, Ba

General Properties

Size

	Be	Mg	Ca	Sr	Ba
Covalent radii (in pm)	89	136	174	192	198
Metallic radii (in pm)	112	160	197	215	224
Ionic size (M ²⁺) (in pm)	31	65	99	113	135

Note : Ca^{2+} (99 pm), Co^{2+} (72 pm), Ni^{2+} (69 pm), Zn^{2+} (74 pm)

- Melting points ($^{\circ}\text{C}$) :

Be	Mg	Ca	Sr	Ba
1287	650	839	770	727

- Density (g/mL) :

Be	Mg	Ca	Sr	Ba
1.84	1.74	1.55	2.63	3.59

Note : Ca has the lowest density amongst alkaline earth metals.

Be, Mg – *hcp*, Ca, Sr – *fcc*, Ba – *bcc*

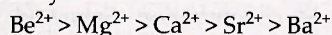
- Standard oxidation potential :

	Be	Mg	Ca	Sr	Ba
E°_{OP} (in volts)	1.85	2.37	2.87	2.89	2.91

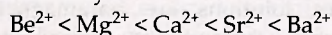
- Specific heats of alkaline earth metals are greater than those of alkali metals.

- Hydrated salts : Due to small size of M^{2+} , the alkaline earth metal salts are extensively hydrated. Examples are $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

Size of hydrated ion decreases as :



- Ionic mobility :



□ General Reactions

	Be	Mg	Ca – Ba
Air	No reaction below 600°C but powdered metal burns to give $\text{BeO} + \text{Be}_3\text{N}_2$	Brilliantly burns to give $\text{MgO} + \text{Mg}_3\text{N}_2$	$\text{MO} + \text{M}_3\text{N}_2$ $\text{Ca} \rightarrow$ mainly nitride $\text{Ba} \rightarrow$ mainly oxide
C	Be_2C at 1700°C	MgC_2 at red heat	MC_2 at red heat
Cold/hot water	No reaction	amalgam reacts to give H_2	$\text{M}(\text{OH})_2 + \text{H}_2$
Steam	No reaction	$\text{MgO} + \text{H}_2$	$\text{M}(\text{OH})_2 + \text{H}_2$
N_2	Be_3N_2 at 1000°C	Mg_3N_2 at $800 - 850^{\circ}\text{C}$	M_3N_2 on gentle heating

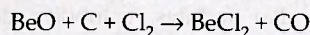
□ Abnormal behaviour of Beryllium

- Be dissolves in aqueous mineral acids (HCl , HNO_3 , H_2SO_4) evolving H_2 , though conc. HNO_3 renders it passive. Also Be dissolves in aqueous caustic alkali forming sodium beryllate, Na_2BeO_2 .
- BeO is amphoteric in nature whereas other oxides are basic.

- Be and Mg do not impart colour to flame.
 - Be and Mg carbonates are not precipitated by $(\text{NH}_4)_2\text{CO}_3$ in presence of NH_4Cl .
 - Be_2C reacts with water to give CH_4 whereas magnesium carbide and calcium carbide give propyne and acetylene respectively.
 - Be^{2+} ions are extensively hydrated in aq. solution. Due to small size of Be^{2+} ion, O – H bonds get weakened and the solution becomes distinctly acidic.
- Note :** Be forms very stable $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ while the other metal ions tend to achieve 6 co-ordination. For example $[\text{Ca}(\text{H}_2\text{O})_6]^{2+}$.

□ Extraction

- Be is extracted from beryl, $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. It is first converted to basic carbonate which is then ignited to BeO . Finally, BeO is heated with 'C' at $600 - 800^{\circ}\text{C}$.



A mixture of BeCl_2 and NaCl is electrolysed at 800°C to obtain Be.

- Mg is extracted by the electrolysis of fused MgCl_2 (+ CaCl_2 + NaCl) at 750°C . 'C' reduction of MgO (2000°C) also give Mg:



Note : MgH_2 decomposes at 250°C and low 'P' to give a highly reactive form of Mg.

- Ca is extracted by electrolysis of fused CaCl_2 (plus CaF_2 to lower the m.pt. from 774°C to 664°C).

Note : Radium is recovered in small quantities from uranium minerals – less than 100 g a year over the world.

□ Uses

- Be is used to improve the properties of Cu – Ni alloys. Mg is largely used as a light weight construction metal.

□ General Chemical Behaviour

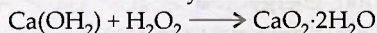
- Oxides, peroxides and hydroxides :

They form monoxides when heated with O_2 . BeO is covalent, others exist as NaCl structure. High charges on both cation and anion give rise to high lattice energy.

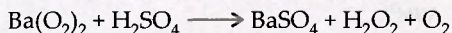
	BeO	MgO	CaO	SrO	BaO
M.pt.	2530	2826	2600	2400	1900

- High polarising power of the smaller cations makes the superoxides and peroxides unstable to heat. However, stability increases with electropositive character and size of metal.

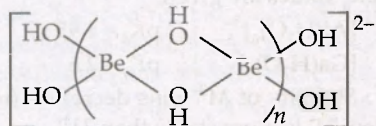
- Hydrated peroxides of Mg, Ca, Sr and Ba may be obtained by adding H_2O_2 into aq. solution of these metal salts or hydroxides.



- Dilute aqueous acids liberate H_2O_2 from peroxides and $\text{H}_2\text{O}_2 + \text{O}_2$ from the superoxides.



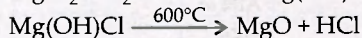
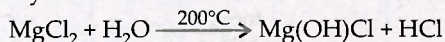
- For hydroxides, solubility in water and basic character increases from $\text{Be}(\text{OH})_2$ to $\text{Ba}(\text{OH})_2$. Being amphoteric in nature, $\text{Be}(\text{OH})_2$ dissolves in excess alkali. The initial solutions believed to consist of polymeric chain.



Further addition of alkali depolymerises the chain to give the mononuclear beryllate, $[\text{Be}(\text{OH})_4]^{2-}$.

- Halides

These are obtained by reacting the halogen hydrides with the metal, its oxide or carbonate. Anhydrous Be and Mg halides cannot be obtained by simply heating the aq. solution owing to hydrolysis.



Anhydrous MgCl_2 can be prepared by heating the hydrate in vacuum at 175°C or in a current of HCl.

BeCl_2 is prepared by heating BeO in CCl_4 vapour at 800°C . Beryllium halides are covalent and polymeric. Do not conduct electricity in molten state.

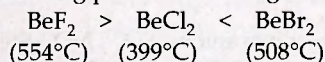
Notes : Except BeF_2 , all other beryllium halides dissolve in polar organic solvents. Anhydrous MgX_2 dissolve in alcohols, ethers and ketones. BeF_2 acts as Lewis acid and exists as glassy solid when 'Be' is 4 co-ordinated. Above 270°C , it adopts crystalline structure.

- Anhydrous BeCl_2 (m.pt. 405°C) is polymeric in solid state. It contains halogen bridges. Be-atoms are in sp^3 -state. In the vapour phase below 1200 K, it exists as dimer and above 1200 K exists as monomer.

- BeF_2 is highly soluble in water. MgF_2 and CaF_2 are almost insoluble. Solubility again increases down. For chlorides, solubility decreases from Mg to Ra.

Notes : In BeF_2 , hydration energy is very high. For BaF_2 , the large cations touch one another. This lowers the lattice energy considerably.

- Melting points of fluorides are much higher than other halides. CaF_2 has very high melting point (1418°C). For beryllium halides, the melting points show irregular trend.



- Except MgF_2 , which has rutile structure, other fluorides have the characteristic fluorite structure. Magnesium and calcium halides readily absorb water while others are normally anhydrous.

- Salts of oxo-acids

The tendency to form hydrates decreases for sulphates, nitrates and carbonates from Be to Ba. The thermal stability increases.

Notes : Strong polarising power of Be^{2+} ion make BeCO_3 unstable.

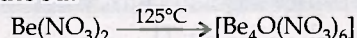
Carbonates	BeCO_3	MgCO_3	CaCO_3	BaCO_3
Decomposition temp.	25°C	420°C	810°C	1280°C

The solubility in water decreases in the order: $\text{Be} > \text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$.

- The sulphates from Ca onwards being practically insoluble. SrSO_4 , BaSO_4 and RaSO_4 are anhydrous.

- High solubility of MgSO_4 is due to loose packing of large sized SO_4^{2-} ions with Mg^{2+} ions.

- Nitrates of group II metals can be obtained by treating the oxides, hydroxides or carbonates with HNO_3 . Crystallisation of the solution gives the hydrated salts. On heating they give oxides but

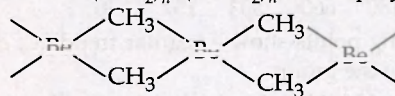


This basic beryllium nitrate has four 'Be'-atoms around the central 'O' and six NO_3 acting as bridging ligands. Similarly, basic beryllium acetate is also known.

- Hydrides

Mg, Ca, Sr and Ba directly react with H_2 to form hydride. BeH_2 is difficult to prepare. BeH_2 is polymeric containing 3c 2e-bonds. In the gas phase, B_3H_2 exists in several forms including polymeric chains and rings.

Note : Like $(\text{BeH}_2)_n$, $(\text{BeMe}_2)_n$ is also polymeric.

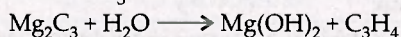


Each 'C' has co-ordination number 5 and each 'Be' is sp^3 .

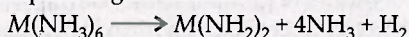
- Complexing tendency : Complexing tendency decreases in the order : $\text{Be} > \text{Mg} > \text{Ca} > \text{Sr}$.
- Stability of such complexes depend on several factors :
 - Stability decreases with increasing size of metal ions for small sized and high charged ions.
 - For larger oxo anions, SO_4^{2-} , NO_3^- , the order is reversed *i.e.*, $\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$.
 - For EDTA, the stability order is $\text{Mg} < \text{Ca} > \text{Sr} > \text{Ba}$.
- Nitrides : All alkaline earth metals burn in N_2 gas to form nitrides (M_3N_2). Be_3N_2 is rather volatile; while others are not. All nitrides are crystalline solids which decompose on heating.

Note : Be_3N_2 is volatile probably because it has greater degree of covalence.

- Carbides : BeO when heated with 'C' at $1900\text{--}2000^\circ\text{C}$ a brick red coloured compound Be_2C is formed. Other members form carbides of formula MC_2 . On heating MgC_2 changes to Mg_2C_3 that contains C_3^{4-} ion.



- Solutions in liquid NH_3 : The metals of group II Ca, Sr, Ba dissolve in liq. NH_3 . The solutions decompose very slowly releasing amides and hydrogen. Evaporation of ammonia solution give group-I metals, but similar evaporation of solution of group-II metals give hexa-ammoniates of the metals. They slowly decompose to give amides.



- Concentrated solutions are bronze coloured due to formation of clusters.

GROUP-III A

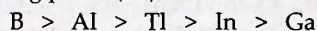
Members : B, Al, Ga, In, Tl

General Properties

- Size :

Covalent radii (in pm)	B	Al	Ga	In	Tl
	82	125	125	150	170
Ionic radii (M^{3+}) (in pm)	B	Al	Ga	In	Tl
	27	50	62	81	95

- Melting points($^\circ\text{C}$) :



2180 660 303 157 30

Boiling points show a regular trend *i.e.*, decrease down the group.

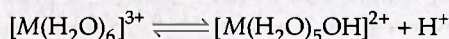
Note : Liquid Ga has higher density than solid Ga, which is an unusual property. Ga exists as liquid in the temperature range 30°C to 2000°C .

- Density : Density gradually increases from B to Tl.
- Ionisation energy : $\text{B} > \text{Tl} > \text{Ga} > \text{Al} > \text{In}$. 2nd IP also follow the same trend.

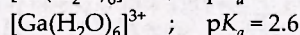
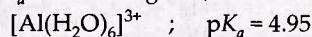
- Standard oxidation potential :

	Al	Ga	In	Tl
$E^\circ_{\text{OP}}(\text{in V}) : \text{M}/\text{M}^{3+}$	1.66	0.56	0.34	-1.26

- Hydration : All the metal ions exist as $[\text{M}(\text{H}_2\text{O})_6]^{3+}$ in water solution. Such aqua ions act as acids due to high polarising power of the cation.



Two $\text{p}K_a$ values are given,



Note : Stability of M^{3+} ions decreases from Al to Tl. Also, Tl^+ is more stable than Tl^{3+} .

General Reactions

	B	Al	Ga	In	Tl
With O_2 at high temperature	B_2O_3	Al_2O_3 (highly exothermic)	Ga_2O_3	In_2O_3	Tl_2O_3 (also Tl_2O)
With N_2	—	only Al forms AlN at high temperature	—	—	—
With $\text{F}_2, \text{Cl}_2, \text{Br}_2$	—	AlX_3	GaX_3	InX_3	TlX_3 (TlX is also formed)
With I_2	—	AlI_3	GaI_3	InI_3	Tl^+I_3^-
With dilute mineral acid	only oxidising acids react	gives Al^{3+}	gives Ga^{3+}	gives In^{3+}	gives Tl^+

Note : Conc. HNO_3 makes Al, Ga, In passive.

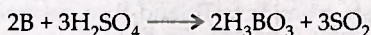
Abnormal behaviour of Boron

Boron is a high melting solid containing B_{12} units. The B_{12} units icosahedron structure, a solid figure with 12 vertices and 20 equilateral triangles.

Crystalline boron is chemically very inert, it is not affected by acids or oxidising agents. Fused NaOH attacks it above 500°C giving NaBO_2 and H_2 .

Oxidising acids like HNO_3 and conc. H_2SO_4 dissolve boron but boron remains inert in its

reaction with HCl.



- Hydrides of boron like hydrides of silicon are spontaneously flammable volatile compounds.
- The common halides of boron and silicon are mostly gases.
- Boron oxide is acidic in nature.

Extraction

- Crystalline boron of high purity is obtained by reduction of volatile boron compounds BCl_3 or BBr_3 with H_2 . On the other hand, when B_2O_3 is reduced with Mg give amorphous boron.
- Aluminium is extracted electrolytically from bauxite. Purified bauxite (melting point 2050°C) is dissolved in cryolite and electrolysed at 950°C . Electrolyte contains 80-85% Al_2O_3 , CaF_2 – 5 to 7%, AlF_3 – 5 to 7%. Li_2CO_3 is also used to lower the melting point.

Uses

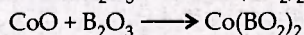
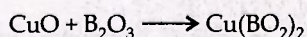
- Boron carbides and metal borides are extensively used as neutron shields and control rods. Cheap, easily malleable, light, non-toxic and fairly corrosion resistant aluminium is widely used. Ga, As is largely used in light emitting diodes.

General Chemical Behaviour

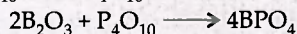
- Oxides and hydroxides : All the members of group 13 form oxides M_2O_3 and hydroxides.

B_2O_3 More acidic less basic	Al_2O_3 and Ga_2O_3 Amphoteric	In_2O_3 and Tl_2O_3 Basic
B(OH)_3 Weakly acidic	Al(OH)_3 and Ga(OH)_3 Amphoteric	In(OH)_3 and Tl(OH)_3 Basic

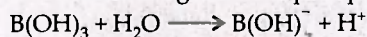
- B_2O_3 combines with metal oxides to form basic metaborates.



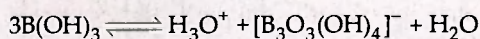
B_2O_3 also combines with acidic oxides such as P_4O_{10} and As_4O_{10} .



Among hydroxides only B(OH)_3 is water soluble. It's a Lewis acid. Rest all hydroxides are insoluble in water and form a gelatinous precipitate.



When concentration of the solution is very high, polymeric metaborates also exist.



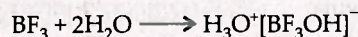
Tl(OH) is water-soluble.

Notes : Boric acid can be titrated with strong alkali using phenolphthalein indicator in presence of glycerol. The later raises its acidity.

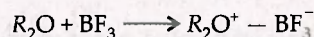
- Halides : All boron trihalides except BF_3 are hydrolysed to boric acid.



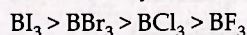
However, BF_3 forms an addition product with H_2O .



Boron halides are Lewis acids.



Lewis acidity decreases in the order



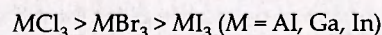
Notes : Stability of ether adducts of BF_3 follow the order : $\text{Me}_2\text{O} > \text{Et}_2\text{O}$

→ B – F bond is longer in BF_3 than as compared to BF_4^- and $(\text{CH}_3)_3\text{N.BF}_3$.

→ 'B' forms BF_4^- , whereas Al, Ga and In form AlF_6^{3-} , GaCl_6^{3-} , InCl_6^{3-} .

The fluorides of Al, Ga, In and Tl are ionic and have high melting points. Other halides of Al, Ga, In and Tl are largely covalent in anhydrous state and possess low melting point. Vapour density of AlCl_3 measured at 400°C corresponding to the formula Al_2Cl_6 . This dimeric structure exists in vapour state below 473 K and at higher temperature dissociates to trigonal planar structure.

Note : Towards $(\text{C}_2\text{H}_5)_2\text{O}$ or $(\text{C}_2\text{H}_5)_3\text{N}$; the acidity order is



Also, towards $(\text{CH}_3)_2\text{S}$ or $(\text{CH}_3\text{CH}_2)_2\text{S}$; the acidity order is $\text{AlCl}_3 > \text{AlBr}_3 > \text{AlI}_3$

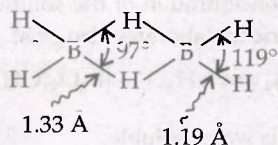
but $\text{MI}_3 > \text{MBr}_3 > \text{MCl}_3$ ($\text{M} = \text{Ga and In}$)

- Hydrides :** Boron hydrides are most important.

Nido-boranes B_nH_{n+4}	Arachno-boranes B_nH_{n+6}
B_2H_6	B_4H_{10}
B_5H_9	B_5H_{11}

B_2H_6 when heated to 120°C , B_4H_{10} is produced.

B_2H_6 :



B – B distance is 1.77 Å.

B_4H_{10} :

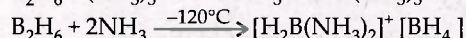
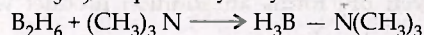
No. of B – H – B bonds = 4

No. of B – B – B bonds = 0

No. of B – B bonds = 1

No. of BH_2 groups = 2

In B_5H_9 , respectively they are 4, 1, 2, 0



Diborane when reduced with NaH, LiH gives BH_4^- .

Notes : $NaBH_4$ can be used as reducing agent in water solvent but $LiAlH_4$ can not.

Transition Elements

Members	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
(3d-series)										

General Properties

Size :

Metallic radii (in pm)	Ionic radii (M^{2+}) : (Pauling in 6 : 6 co-ordination number)
Sc 164	Sc –
Ti 147	Ti –
V 135	V –
Cr 129	Cr –
Mn 137	Mn 80
Fe 126	Fe 75
Co 125	Co 72
Ni 125	Ni 69
Cu 128	Cu –
Zn 137	Zn 74

Note : Different methods of measurement have reported different results. For example, Shannon and Prewitt method reports Zn^{2+} ion radius in 6 : 6 co-ordination sphere as 88 pm.

- Ionisation potential : 1st ionisation potential increases from Sc to Fe and then decreases. Zinc has the highest 1st I.P. while Sc has the lowest in 3d-series.

$Zn > Fe > Co > Cu > Ni$

2nd I.P. is highest for Cu followed by Ni and then Zn. Again it is lowest for Sc.

- Melting point : $W > Re > Os > Cr > Fe > Sc > Mn$
- Standard electrode potential

M^{n+}/M	T	V	Cr	Mn
(in V)	–1.13			
	Fe	Co	Ni	Cu
	–0.44	–0.28	–0.26	+0.34

E° values for Mn, Ni and Zn are more negative than expected due to stability of half-filled Mn^{2+} , and completely filled Zn^{2+} nature. In Ni, the reason is highest enthalpy of hydration for Ni^{2+} ion.

Note : Mn^{3+} and Co^{3+} ions are the strongest oxidants in aqueous solution. On the other hand, V^{2+} and Cr^{2+} are strong reducing agents.

- Stabilisation of oxidation states : Stability is a relative term, meaningful only when referred to a given set of conditions. Compounds containing Cu(I) are thermally stable, but in aqueous solution Cu^+ readily disproportionates into Cu^0 and Cu^{2+} . In presence of cyanide, however, Cu^+ can be stabilised in aqueous solution. High oxidation states are favoured by alkaline media. Low oxidation states are stabilised by reducing solvents.

Note : If the low oxidation state gets oxidised somehow, the reducing solvent will again force it back to the original oxidation state.

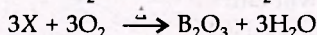
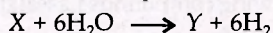
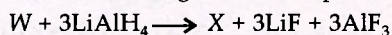
- Oxides : V_2O_5 , CrO_3 – acidic
 CuO , ZnO , Cr_2O_3 , CrO_2 , VO_2 , TiO_2 and Fe_2O_3 – amphoteric.
- Halides : $CuCl_2$ and $CuBr_2$ consists of infinite chlorine or bromine bridges with co-ordination number 6.
Their halides in higher oxidation states are relatively unstable and undergo hydrolysis. Strongly reducing states probably do not form fluorides while strongly oxidising states form fluorides but not iodides.

TiF_2 is not known because Ti^{2+} is easily oxidised to Ti^{4+} and is strongly reducing agent. Similarly, VF_4 is known but VI_4 is not.

NCERT Xtract

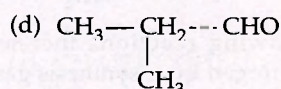
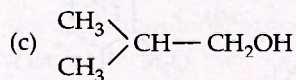
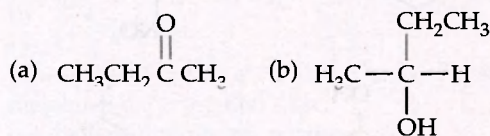
Questions for NEET

1. Of the following chemical equations.



Identify W, X, Y respectively.

- (a) $\text{Na}_2\text{B}_4\text{O}_7$, H_3BO_3 , B_2O_3
 (b) H_3BO_3 , B_2H_6 , BF_3
 (c) BF_3 , B_2H_6 , H_3BO_3
 (d) H_3BO_3 , $\text{Na}_2\text{B}_4\text{O}_7$, B_2O_3
2. A hydrocarbon 'P', (C_4H_8) on reaction with HCl gives a compound 'Q', ($\text{C}_4\text{H}_9\text{Cl}$), which on reaction with 1 mol of NH_3 gives compound 'R', ($\text{C}_4\text{H}_{11}\text{N}$). On reacting with NaNO_2 and HCl followed by treatment with water, compound 'R' yields an optically active alcohol, 'S'. Ozonolysis of 'P' gives 2 mol of acetaldehyde. Identify compound 'S'.



3. Lifetimes of the molecules in the excited states are often measured by using pulsed radiation source of duration nearly in the nano-second range. If the radiation source has the duration of 2 ns and the number of photons emitted during the pulse source is 2.5×10^{15} , calculate the energy of the source.

- (a) $1.65 \times 10^{-10} \text{ J}$ (b) $8.28 \times 10^{-10} \text{ J}$
 (c) $0.5 \times 10^9 \text{ J}$ (d) $1.65 \times 10^{-19} \text{ J}$

4. Calculate the mole fraction of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) in a solution containing 20% of $\text{C}_2\text{H}_6\text{O}_2$ by mass.
 (a) 0.932 (b) 0.862 (c) 0.950 (d) 0.779
5. Table-tennis ball has a mass 10 g and a speed of 90 m/s. If speed can be measured within an accuracy of 4%. What will be the uncertainty in speed and position?
 (a) $6.626 \times 10^{-34} \text{ m}$ (b) $4 \times 10^{-32} \text{ m}$
 (c) $1.46 \times 10^{-33} \text{ m}$ (d) $0.6 \times 0.6 \times 10^{-31} \text{ m}$
6. In which pair most efficient packing is present?
 (a) *hcp* and *bcc* (b) *hcp* and *ccp*
 (c) *bcc* and *ccp*
 (d) *bcc* and simple cubic cell.
7. Quartz is extensively used as a piezoelectric material, it contains
 (a) Pb (b) Si (c) Ti (d) Sn
8. X-ray diffraction studies show that copper crystallises in an *fcc* unit cell with cell edge of $3.608 \times 10^{-8} \text{ cm}$. In a separate experiment, copper is determined to have a density of 8.92 g/cm^3 , calculate the atomic mass of copper.
 (a) 60.1 u (b) 63.1 u
 (c) 69.3 u (d) 62.7 u
9. $2P + 3Q \longrightarrow 2R$
 In which of the following reaction mixtures, P is the limiting reagent?
 (a) 5 mol P + 2.5 mol Q
 (b) 3 mol P + 7 mol Q
 (c) 4 mol P + 1 mol Q
 (d) 6 mol P + 5 mol Q

10. Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100Ω . If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520Ω , calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 mol L^{-1} KCl solution is 1.29 S/m .

- (a) $124 \times 10^3 \text{ S m}^2 \text{ mol}^{-1}$
 (b) $124 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$
 (c) $124 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
 (d) $124 \times 10^4 \text{ S m}^2 \text{ mol}^{-1}$

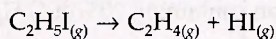
11. Which of the following dissolves in hot conc. NaOH?

- (a) Fe (b) Zn (c) Cu (d) Ag.

12. pH of a solution of a strong acid is 5.0. What will be the pH of the solution obtained after diluting the given solution 100 times?

- (a) 6.6 (b) 2.7 (c) 7 (d) 3.01

13. The first order rate constant for the decompositions of ethyl iodide by the reaction



at 600 K is $1.60 \times 10^{-5} \text{ s}^{-1}$. Its energy of activation is 209 kJ/mol . Calculate the rate constant of the reaction at 700 K .

- (a) $6.36 \times 10^{-3} \text{ s}^{-1}$ (b) $6.24 \times 10^{-3} \text{ s}^{-1}$
 (c) $6.57 \times 10^{-3} \text{ s}^{-1}$ (d) $6.86 \times 10^{-3} \text{ s}^{-1}$

14. The first ionisation energies of the elements of the first transition series (Ti \rightarrow Cu)

- (a) increase as the atomic number increases
 (b) decrease as the atomic number increases
 (c) do not show any change as the addition of electrons takes place in the inner $(n-1)$ d-orbitals
 (d) increase from Ti to Mn and then decreases from Mn to Cu.

15. 20 mL of 0.2 M BaCl_2 is mixed with 30 mL of $0.3 \text{ M Al}_2(\text{SO}_4)_3$. The weight of BaSO_4 formed is

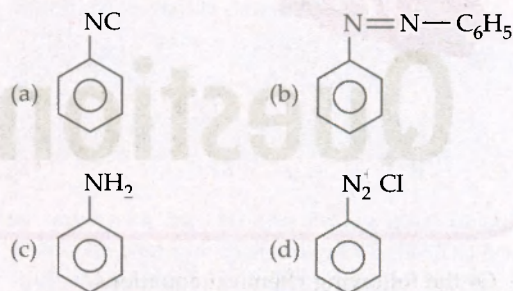
- (a) 0.932 g (b) 0.233 g
 (c) 0.699 g (d) 0.116 g

16. Which one of the following is a case of adsorption?

- (a) Silica gel in contact with water vapour.
 (b) Cotton cloth dipped in a dye solution.
 (c) Anhydrous CuSO_4 in contact with water vapour.
 (d) Ammonia gas in contact with water.

17. A colourless substance 'P' ($\text{C}_6\text{H}_7\text{N}$) is sparingly soluble in water and gives a water soluble compound 'Q' on treating with mineral acid.

On reacting with CHCl_3 and alcoholic potash 'P' produces an obnoxious smell due to the formation of compound 'R'. Reaction of 'P' with benzenesulphonyl chloride gives compound 'S' which is soluble in alkali. With NaNO_2 and HCl , 'P' forms compound 'T' which reacts with phenol in alkaline medium to give an orange dye 'U'. Identify compound 'T'.



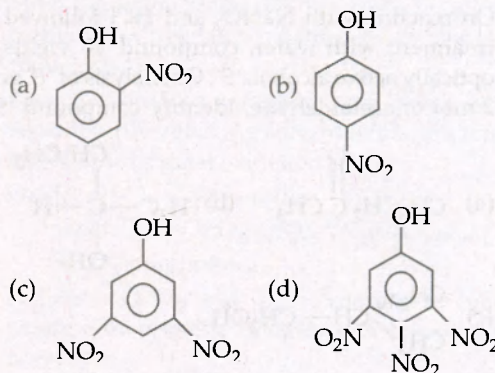
18. For which of the following compounds Lassaigne's test of nitrogen will fail?

- (a) $\text{H}_2\text{NCONH.NH}_2 \cdot \text{HCl}$
 (b) $\text{H}_2\text{NNH}_2 \cdot 2\text{HCl}$
 (c) H_2NCONH_2
 (d) $\text{C}_6\text{H}_5 - \text{N} = \text{N} - \text{C}_6\text{H}_5$

19. The metals present in insulin, haemoglobin and vitamin B_{12} are respectively

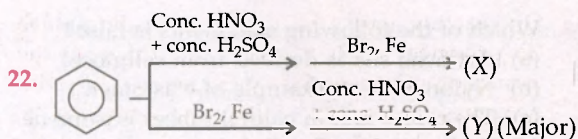
- (a) Zn, Hg, Cr (b) Co, Fe, Zn
 (c) Mg, Fe, Co (d) Zn, Fe, Co

20. The most steam volatile compound is

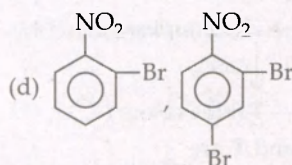
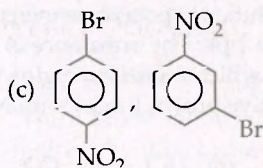
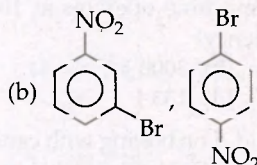
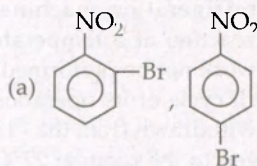


21. Which of the following reactions increases production of dihydrogen from synthesis gas?

- (a) $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \xrightarrow[\text{Ni}]{1270 \text{ K}} \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$
 (b) $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \xrightarrow{1270 \text{ K}} \text{CO}(\text{g}) + \text{H}_2(\text{g})$
 (c) $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \xrightarrow[\text{Catalyst}]{673 \text{ K}} \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$
 (d) $\text{C}_2\text{H}_6 + 2\text{H}_2\text{O} \xrightarrow[\text{Ni}]{1270 \text{ K}} 2\text{CO} + 5\text{H}_2$



then, the products (X) and (Y) will be



23. The following data are obtained when carbon and dioxygen react together to form different compounds.

Mass of carbon	Mass of oxygen
(i) 12 g	16 g
(ii) 12 g	32 g

Which law of chemical combination is obeyed by the above experimental data?

- (a) Law of definite proportions
 (b) Law of multiple proportions
 (c) Gay Lussac's law of gaseous volumes
 (d) Avogadro law.

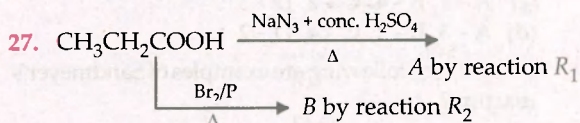
24. The correct order of acidic strength is

- (a) $\text{CH}_3\text{CF}_2\text{COOH} > \text{CH}_3\text{CCl}_2\text{COOH} > \text{CH}_3\text{CBr}_2\text{COOH}$
 (b) $\text{CH}_3\text{CF}_2\text{COOH} > \text{CH}_3\text{CBr}_2\text{COOH} > \text{CH}_3\text{CCl}_2\text{COOH}$
 (c) $\text{CH}_3\text{CBr}_2\text{COOH} > \text{CH}_3\text{CCl}_2\text{COOH} > \text{CH}_3\text{CF}_2\text{COOH}$
 (d) $\text{CH}_3\text{CCl}_2\text{COOH} > \text{CH}_3\text{CBr}_2\text{COOH} > \text{CH}_3\text{CF}_2\text{COOH}$


25. Which of the following statements is incorrect?
 (a) Helium has the highest first ionisation enthalpy in the periodic table.
 (b) Chlorine has less negative electron gain enthalpy than fluorine.
 (c) Mercury and bromine are liquids at room temperature.
 (d) In any period, atomic radius of alkali metal is the highest.

26. Which of the following ore is the best concentrated by froth floatation method?

- (a) Galena (b) Cassiterite
 (c) Malachite (d) Magnetite

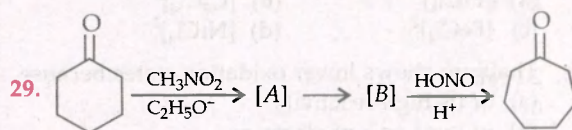


Which is correct alternate?

- | | | | |
|---|--|---------|---------|
| A | B | R_1 | R_2 |
| (a) $\text{CH}_3\text{CH}_2\text{NH}_2$ |  | Schmidt | HVZ |
| (b) $\text{CH}_3\text{CH}_2\text{CONH}_2$ | $\text{CH}_3\text{CH}_2\text{COBr}$ | HVZ | Schmidt |
| (c) $\text{CH}_3\text{CH}_2\text{NH}_2$ | $\text{CH}_3\text{CH}_2\text{COBr}$ | HVZ | Schmidt |
| (d) None is correct. | | | |

28. Hydrolysis of one mole of peroxodisulphuric acid produces

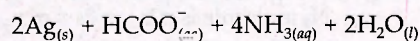
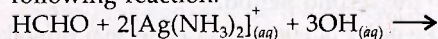
- (a) two moles of sulphuric acid
 (b) two moles of peroxomonosulphuric acid
 (c) one mole of sulphuric acid and one mole of peroxomonosulphuric acid
 (d) one mole each of sulphuric acid, peroxomonosulphuric acid and hydrogen peroxide.



Which reaction is/are involved in the above conversion?

- (a) Diazotisation and Beckmann rearrangement.
 (b) Diazotisation and Robinson annulation.
 (c) Aldol condensation and diazotisation.
 (d) Diazotisation and pinacol type of rearrangement.

30. Select the species which is reduced in the following reaction.



- (a) HCHO (b) $[\text{Ag}(\text{NH}_3)_2]^+$
(c) NH_3 (d) Ag
31. Match list I with list II and select the answer using the codes given below :

List I	List II
A XeF_4	1 Distorted octahedral
B XeF_6	2 Tetrahedral
C XeO_3	3 Square planar
D XeO_4	4 Trigonal pyramidal

- (a) A - 4, B - 1, C - 3, D - 2
(b) A - 2, B - 3, C - 1, D - 4
(c) A - 1, B - 4, C - 2, D - 3
(d) A - 3, B - 1, C - 4, D - 2
32. Which of the following are examples of Sandmeyer's reaction?
- (a) $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- \xrightarrow{\text{CuCl}} \text{C}_6\text{H}_5\text{Cl}$
(b) $\text{C}_6\text{H}_5\text{Cl} \xrightarrow{\text{Cu}_2(\text{CN})_2} \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$
(c) $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- \xrightarrow{\text{NaNO}_2/\text{Cu}/\Delta} \text{C}_6\text{H}_5\text{NO}_2$
(d) $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- \xrightarrow{\text{KI}/\Delta} \text{C}_6\text{H}_5\text{I}$
33. Reaction of glucose with acetic anhydride indicates the presence of
(a) $-\text{CHO}$ group (b) $-\text{CH}_2-$ group
(c) five $-\text{OH}$ groups (d) all of these.
34. The molecules of a gas A travel four times faster than the molecules of gas B at the same temperature. The ratio of molecular weights M_A/M_B will be
(a) 1/16 (b) 4 (c) 1/4 (d) 16.
35. Which of the following has a square planar geometry?
(a) $[\text{PtCl}_4]^{2-}$ (b) $[\text{CoCl}_4]^{2-}$
(c) $[\text{FeCl}_4]^{2-}$ (d) $[\text{NiCl}_4]^{2-}$
36. Thallium shows lower oxidation states because
(a) of its high reactivity
(b) of inert pair of electrons
(c) of its amphoteric nature
(d) it is a transition metal.
37. Which of the following statements is not correct from the view point of the molecular orbital theory?
(a) Be_2 is not a stable molecule.
(b) He_2 is not stable but He_2 is expected to exist.
(c) Bond strength of N_2 is maximum amongst the homonuclear diatomic molecules belonging to the second period.
(d) The order of energies of molecular orbitals in N_2 molecule is $\sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$

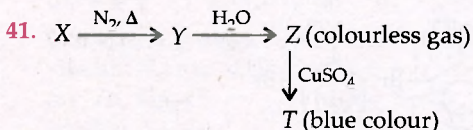
38. Which of the following statements is false?
(a) Artificial silk is derived from cellulose.
(b) Nylon-66 is an example of elastomer.
(c) The repeat unit in natural rubber is isoprene.
(d) Both starch and cellulose are polymers of glucose.

39. A scientist needs a refrigeration machine to maintain a chemical reaction at a temperature of -13°C . How much work not be performed on the system during each cycle of its operation if 3000 J of heat is to be withdrawn from the -13°C reservoir and discharged to the room at 27°C in each cycle. (Assume machine operates at 100% of its theoretical efficiency)

- (a) 65000 J (b) 3000 J
(c) 154 J (d) 133 J

40. A white crystalline solid A on boiling with caustic soda solution gave a gas B which when passed through an alkaline solution of potassium mercuric iodide gave a brown ppt. The substance A on heating gave a gas C which rekindled a glowing splinter but did not give brown fumes with NO. The gas B is

- (a) H_2S (b) NH_3 (c) HCl (d) CO_2



The substances Y and T are

- (a) $\text{Y} = \text{Mg}_3\text{N}_2$ and $\text{T} = \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
(b) $\text{Y} = \text{Mg}_3\text{N}_2$ and $\text{T} = \text{CuSO}_4 \cdot 4\text{NH}_3$
(c) $\text{Y} = \text{Mg}(\text{NO}_3)_2$ and $\text{T} = \text{CuO}$
(d) $\text{Y} = \text{MgO}$ and $\text{T} = \text{CuSO}_4 \cdot 4\text{NH}_3$

42. A sample of air consisting of N_2 and O_2 was heated at 2500 K until the equilibrium

$$\text{N}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{NO}_{(g)}$$

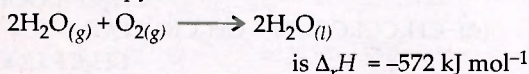
 was established with an equilibrium constant $K_c = 2.1 \times 10^{-3}$. At equilibrium, the mole % of NO was 1.8. Estimate the initial composition of air in mole fraction of N_2 and O_2 .

- (a) 50%, 50% (b) 75%, 25%
(c) 79%, 21% (d) 85%, 15%

43. Which of the following is useful as water softner?

- (a) Thiokol (b) Bakelite
(c) Melamine formaldehyde resin
(d) Ion exchange resins

44. The enthalpy of reaction



What will be standard enthalpy of formation of $\text{H}_2\text{O}_{(l)}$?

- (a) -572 kJ mol^{-1} (b) 286 kJ/mol
(c) $+572 \text{ kJ mol}^{-1}$ (d) -286 kJ/mol

45. Which one of the following is an outer orbital complex and exhibits paramagnetic behaviour?

- (a) $[\text{Ni}(\text{NH}_3)_6]^{2+}$ (b) $[\text{Zn}(\text{NH}_3)_6]^{2+}$
(c) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ (d) $[\text{Co}(\text{NH}_3)_6]^{3+}$

46. When SO_2 is passed through a solution of potassium iodate, the oxidation state of iodine changes from

- (a) $+5$ to 0 (b) $+5$ to -1
(c) -5 to 0 (d) -7 to -1

47. $\text{CH}_2=\text{CHCH}_3 + \text{PCl}_5 \rightarrow \text{A,}$



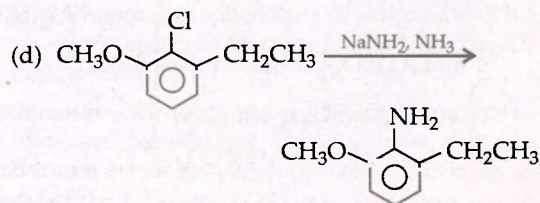
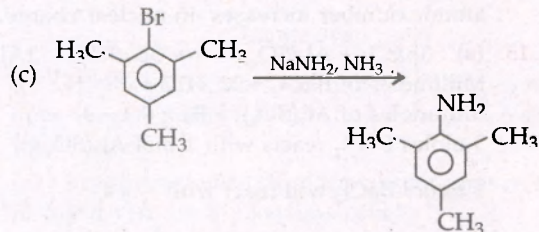
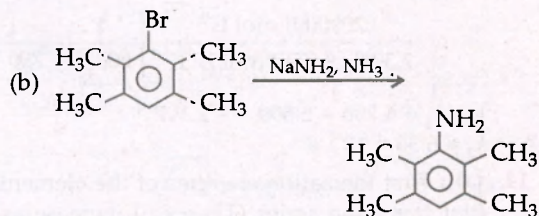
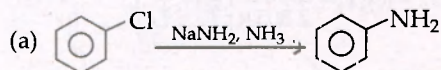
$\text{CH}_3\text{CH}_2\text{CHO} + \text{PCl}_5 \rightarrow \text{B, A and B are}$

- (a) *vic* dihalides (b) *gem* dihalides
(c) A *gem* dihalide, B *vic* dihalide
(d) A *vic* dihalide, B *gem* dihalide

48. Which of the following elements does not form hydride by direct heating with dihydrogen?

- (a) Be (b) Mg (c) Sr (d) Ba

49. Which of the following reactions is feasible?



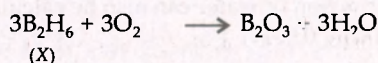
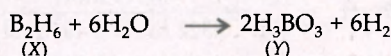
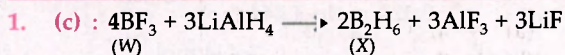
50. Atmospheric pressures recorded in different cities are as follows:

Cities	Shimla	Bangalore	Delhi	Mumbai
p in N/m^2	1.01×10^5	1.2×10^5	1.02×10^5	1.21×10^5

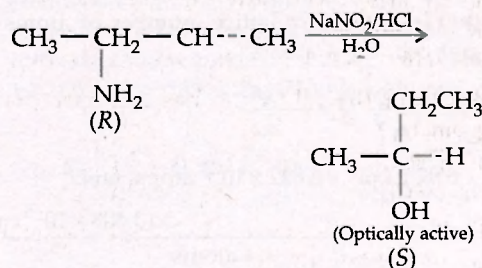
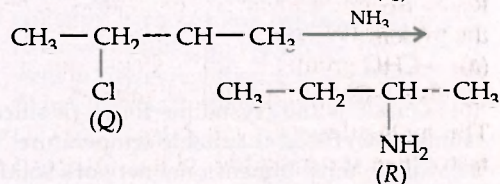
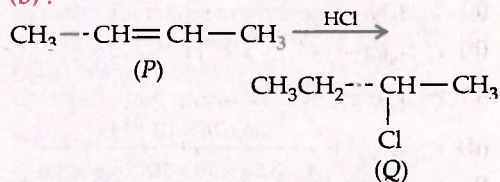
Consider the above data and mark the place at which liquid will boil first.

- (a) Shimla (b) Bangalore
(c) Delhi (d) Mumbai.

SOLUTIONS



2. (b) :



3. (b) : Given that period = $2 \text{ ns} = 2 \times 10^{-9} \text{ s}$, the frequency

$$\text{Frequency} = \frac{1}{\text{Period}} = \frac{1}{2 \times 10^{-9} \text{ s}} = 0.5 \times 10^9 \text{ s}^{-1}$$

Given that $N = 2.5 \times 10^{15}$, energy is

$$E = Nh\nu = 2.5 \times 10^{15} \times 6.626 \times 10^{-34} \times 0.5 \times 10^9 = 8.28 \times 10^{-10} \text{ J}$$

4. (a) : Assume that we have 100 g of solutions (one can start with any amount of solution because the results obtained will be the same). Solution will contain 20 g of ethylene glycol and 80 g of water. Molar mass of $\text{C}_2\text{H}_6\text{O}_2 = 12 \times 2 + 1 \times 6 + 16 \times 2 = 62 \text{ g mol}^{-1}$.

$$\text{Moles of } C_2H_6O_2 = \frac{20 \text{ g}}{62 \text{ g mol}^{-1}} = 0.322 \text{ mol}$$

$$\text{Moles of water} = \frac{80 \text{ g}}{18 \text{ g mol}^{-1}} = 4.444 \text{ mol}$$

$$x_{\text{glycol}} = \frac{\text{mole of } C_2H_6O_2}{\text{moles of } C_2H_6O_2 + \text{moles of } H_2O} = \frac{0.322 \text{ mol}}{0.322 \text{ mol} + 4.444 \text{ mol}} = 0.068$$

$$\text{Similarly, } x_{\text{water}} = \frac{4.444 \text{ mol}}{0.322 \text{ mol} + 4.444 \text{ mol}} = 0.932$$

Mole fraction of water can also be calculated as:
 $1 - 0.068 = 0.932$

5. (c) : The uncertainty in the speed is 4 %, i.e.,

$$90 \times \frac{4}{100} = \frac{18}{5} = 3.6 \text{ m s}^{-1}$$

Using the formula,

$$\Delta x = \frac{h}{4\pi m \Delta v} = \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.14 \times 10 \times 10^{-3} \text{ kg} \times 3.6} = 1.46 \times 10^{-33} \text{ m}$$

6. (b)

7. (b) : Quartz is the crystalline forms of silica. It is interconvertible at suitable temperature. It is a covalent, three-dimensional network solid.

8. (b) : In case of fcc lattice, number of atoms per unit cell, $Z = 4$ atoms

$$\text{Therefore, } M = \frac{dN_A a^3}{Z}$$

$$= \frac{8.92 \text{ g cm}^3 \times 6.022 \times 10^{23} \text{ atoms mol}^{-1}}{4 \text{ atoms}} \times (3.608 \times 10^{-8} \text{ cm})^3$$

$$= 63.1 \text{ g/mol}$$

Atomic mass of copper = 63.1 u

9. (b)

10. (c) : The cell constant is given by the equation:
 Cell constant = G^* = conductivity \times resistance
 $= 1.29 \text{ S/m} \times 100 \Omega = 129 \text{ m}^{-1} = 1.29 \text{ cm}^{-1}$
 Conductivity of 0.02 mol L^{-1} KCl solution = cell constant / resistance

$$= \frac{G^*}{R} = \frac{129 \text{ m}^{-1}}{520 \Omega} = 0.248 \text{ S m}^{-1}$$

$$\text{Concentration} = 0.02 \text{ mol } L^{-1}$$

$$= 1000 \times 0.02 \text{ mol m}^{-3} = 20 \text{ mol m}^{-3}$$

$$\text{Molar conductivity} = \Lambda_m = \frac{K}{c} = \frac{248 \times 10^{-3} \text{ S m}^{-1}}{20 \text{ mol m}^{-3}} = 124 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

11. (b) : $Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$
 Sodium zincate

12. (a) : pH = 5, $[H^+] = 10^{-5} \text{ mol } L^{-1}$
 On 100 times dilution, $[H^+] = 10^{-7} \text{ mol } L^{-1}$
 $\therefore \text{pH} = 7$

It is not possible. This indicates that solution is very dilute. Hence,

Total hydrogen ion concentration, $[H^+]$

$$= \left[\begin{array}{c} \text{Contribution of } H_3O^+ \text{ ion concentration of acid} \end{array} \right] + \left[\begin{array}{c} \text{Contribution of } H_3O^+ \text{ ion concentration of water} \end{array} \right]$$

$$= 10^{-7} + 10^{-7}$$

$$\text{pH} = 2 \times 10^{-7} = 7 - \log 2 = 7 - 0.3010 = 6.6990$$

13. (a) : We know that

$$\log k_2 - \log k_1 = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log k_2 - \log k_1 + \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$= \log(1.60 \times 10^{-5})$$

$$\frac{209000 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left[\frac{1}{600 \text{ K}} - \frac{1}{700 \text{ K}} \right]$$

$$\log k_2 = 4.796 + 2.599 = -2.197$$

$$k_2 = 6.36 \times 10^{-3} \text{ s}^{-1}$$

14. (a) : First ionisation energies of the elements of first transition series (Ti \rightarrow Cu) increase as the atomic number increases in nuclear charge.

15. (a) : $3BaCl_2 + Al_2(SO_4)_3 \rightarrow 3BaSO_4 + 2AlCl_3$

$$\text{Millimoles of } BaCl_2 = 20 \times 0.2 = 4$$

$$\text{Millimoles of } Al_2(SO_4)_3 = 30 \times 0.3 = 9$$

$$3 \text{ moles } BaCl_2 \text{ reacts with } 1 \text{ mol } Al_2(SO_4)_3$$

$$4 \text{ mmol } BaCl_2 \text{ will react with } \frac{1}{3} \times 4$$

$$= \frac{4}{3} \text{ mmol } Al_2(SO_4)_3$$

$$1 \text{ mol } Al_2(SO_4)_3 \text{ forms } 3 \text{ moles } BaSO_4$$

$$\frac{4}{3} \text{ mmol } Al_2(SO_4)_3 \text{ will form } \frac{3}{1} \times \frac{4}{3} \text{ mmol } BaSO_4$$

$$= 4 \text{ mmol } BaSO_4$$

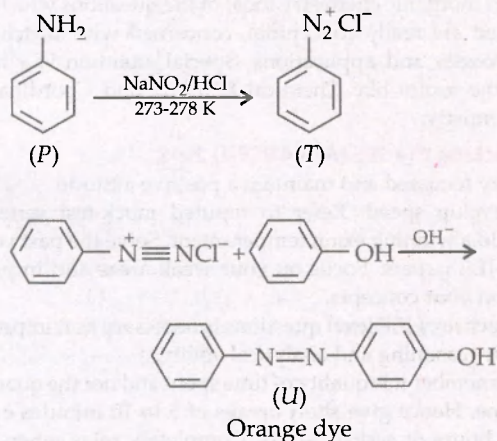
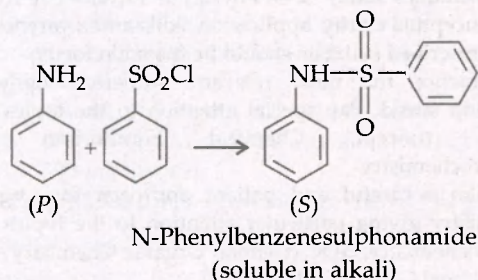
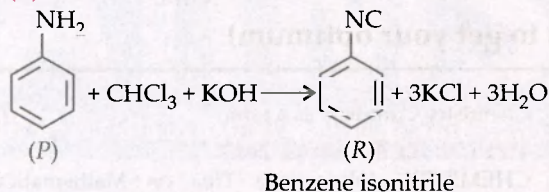
$$\therefore \text{Millimole of } BaSO_4 \text{ formed} = 4$$

$$w = \frac{\text{millimole} \times \text{molecular wt.}}{1000}$$

$$w = \frac{4 \times 233}{1000} = 0.932 \text{ g.}$$

16. (a) : Silica gel adsorbs water.

17. (d) :

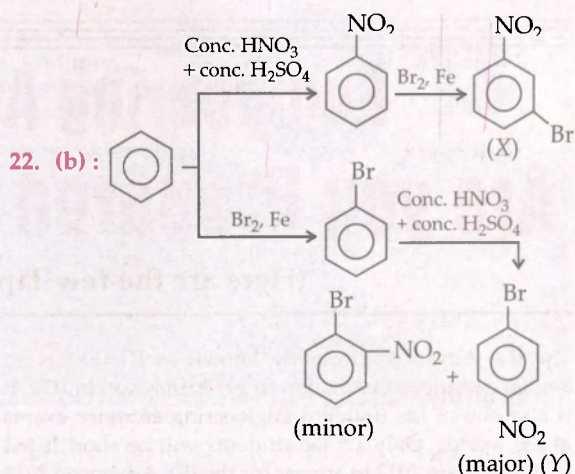


18. (b) : $\text{H}_2\text{NNH}_2 \cdot 2\text{HCl}$ does not contain carbon, hence does not give positive results for Lassaigne's test for nitrogen.

19. (d) : Insulin contains zinc, haemoglobin contains iron and vitamin B_{12} contains cobalt.

20. (a) : In ortho-nitrophenol, $-\text{OH}$ is linked to $-\text{NO}_2$ by means of intramolecular H-bonding. So, it is highly volatile.

21. (c) : The production of dihydrogen can be increased by reacting CO of syngas mixtures with steam in the presence of iron chromate as catalyst.



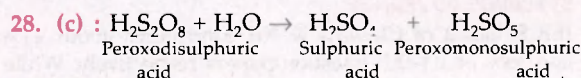
22. (b) : Here, carbon and oxygen combines to form two compounds, carbon monoxide and carbon dioxide. The masses of oxygen (*i.e.*, 16 g and 32 g) which combine with a fixed mass of carbon (12 g) bear a simple ratio, *i.e.*, 16 : 32 or 1 : 2 which obeys the law of multiple proportions.

24. (a)

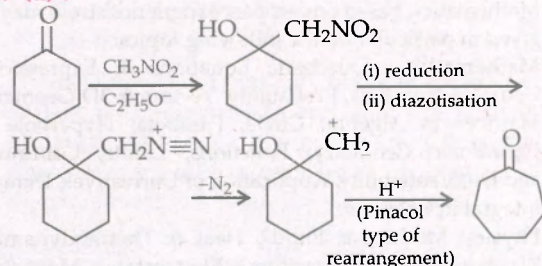
25. (b) : Generally, within a group, electron gain enthalpy becomes less negative down a group. However, adding an electron to the $2p$ -orbital (F) leads to greater repulsion than $3p$ -orbital (Cl). Hence, Cl has the most negative electron gain enthalpy.

26. (a) : Here only galena is PbS (a sulphide ore). Cassiterite is SnO_2 (oxide ore). Magnetite is Fe_3O_4 (oxide ore) and malachite is $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$ (carbonate ore). The froth floatation process is used to concentrate sulphide ores, based on preferential wetting properties with frothing agent and water.

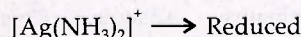
27. (a)



29. (d) :



30. (b) : $\text{HCHO} \rightarrow$ Oxidised



31. (d) : Xe in XeF_4 , XeF_6 , XeO_3 and XeO_4 possesses sp^3d^2 , sp^3d^3 , sp^3 and sp^3 hybridisation respectively.

Contd. on page no. 91

Engineering Aspirants 2013 – Are you Prepared for JEE Advanced?

(Here are the few Tips to get your optimum)

The JEE Advanced (formerly known as IIT-JEE) is an annual entrance examination to get Admission in IITs. It is also one of the toughest engineering entrance exams in the world. Only 1.5 lac students will be short listed from JEE Main 2013 to appear for the JEE Advanced 2013 on June 2nd, 2013. A serious aspirant ideally must have completed the syllabus by now.

Schedule of JEE (Advanced), 2013

The examination will be held on Sunday, June 02, 2013 as per the schedule given below:

Paper 1 9:00 to 12:00 hrs. (IST)

Paper 2 14:00 to 17:00 hrs. (IST)

EXAMINATION PATTERN:

There will be two question papers, each of three hours duration. Both the question papers will consist of three separate sections on Chemistry, Physics and Mathematics. Questions will be of objective type, designed to test comprehension, reasoning and analytical ability of Students.

All the questions will be Multiple Choice Type (MCQ) Negative marking scheme will be followed in the checking of examinations.

A Student can opt for question paper in any of the language viz. English or Hindi.

SYLLABUS COVERAGE:

JEE Syllabus of Class XI & XII contributes about 45% and 55% of IIT-JEE question-papers respectively. While preparing all the chapters of Physics, Chemistry and Mathematics, based on our past experience stress may be given in particular on the following topics:

Mathematics : Quadratic Equations & Expressions, Complex Numbers, Probability, Vectors & 3D Geometry, Matrices in Algebra; Circle, Parabola, Hyperbola in Coordinate Geometry; Functions, Limits, Continuity and Differentiability, Application of Derivatives, Definite Integral in Calculus.

Physics: Mechanics, Fluids, Heat & Thermodynamics, Waves and Sound, Capacitors & Electrostatics, Magnetism, Electromagnetic Induction, Optics and Modern Physics.

Chemistry: Qualitative Analysis, Coordination Chemistry & Chemical Bonding in Inorganic Chemistry, Electrochemistry, Thermodynamics, Chemical Equilibrium in Physical Chemistry and Organic

Chemistry Complete as a topic.

TIPS FOR JEE Advanced, 2013:

CHEMISTRY (please see Tips on Mathematics in 'Mathematics Today' & on Physics in 'Physics For You')

1. Conceptual clarity, application skills and awareness to the prescribed syllabus should be the main focus.
2. Practice the most relevant numerical daily to develop speed. Pay special attention to the topics like Mole concept, Chemical Equilibrium and Electrochemistry.
3. Take a careful and patient approach for Organic chemistry giving particular attention to the topics like Stereochemistry, GOC (General Organic Chemistry) and Functional Group Analysis.
4. In Inorganic chemistry most of the questions which are asked are really conceptual, concerned with structures, processes and applications. Special attention is a must to the topics like Chemical Bonding and Coordination Chemistry.

Cracking the JEE (ADVANCED) 2013

*Stay focussed and maintain a positive attitude

*Develop speed. Refer to reputed mock-test series to build a winning exam temperament. Solve the past year's IIT-JEE papers. Focus on your weak areas and improve upon your concepts.

*Practise of JEE level questions is necessary as it improves your reasoning and analytical ability.

*Remember it is quality of time spent and not the quantity alone. Hence give short breaks of 5 to 10 minutes every 1-2 hours of serious study. Completely relax when you take a break. Practice meditation to develop inner calm, poise, confidence and power of concentration.

*Don't overstress yourself. Five to six hours of sleep every night is a must, especially three-four days before IIT-JEE to keep you physically and mentally fit. While short naps may help to regain freshness, avoid over-sleeping during the day.

*Finally, don't be nervous if you find the paper tough since it is the relative performance that counts. Put your best analytical mind to work, and believe in your preparation.

Authored by Ramesh Batlish, FIITJEE Expert

PRACTICE PAPER

2 Q 13

AIIMS

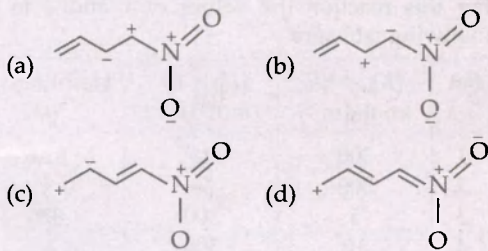
All India Institute of Medical Sciences

Exam on
1st June
2013

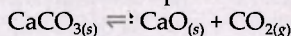
1. You have different HCl solutions having concentration 3 M and 1 M respectively. How many mL of both solutions should be mixed to form 1 L of 1.2 M ?

- 900 mL of 1 M and 100 mL of 3 M
- 100 mL of 1 M and 900 mL of 3 M
- 500 mL of each
- 333.33 mL of 3 M and 666.66 mL of 1 M

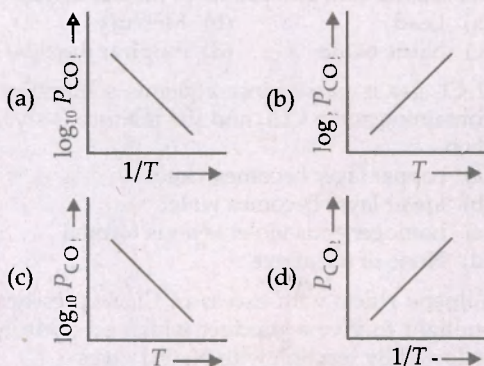
2. Among the following, the least stable resonance structure is



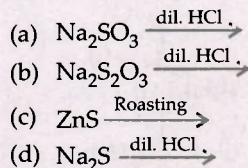
3. For the chemical equilibrium



ΔH°_r can be determined from which one of the following plots?



4. In which of the following reaction, SO_2 gas is not released?



5. A sample of liquid in a thermally insulated container is stirred for 1 hr by a mechanical attachment to a motor in the surroundings, which of the following thermodynamic quantity for the system is zero?

- Work (W)
- Change in internal energy (ΔE)
- Change in enthalpy (ΔH)
- None of these.

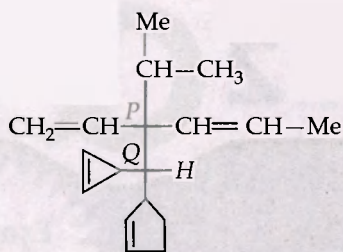
6. In brown ring Fe and NO exist as Fe^+ and NO^+ rather than Fe^{2+} and NO. These forms can be differentiated by

- measuring the conductivity of an aqueous solution of the complex
- by careful crystallization of the complex under special conditions and measuring the magnetic moment in solid state
- estimating the concentration of iron
- determining elevation in boiling point using the complex as solute.

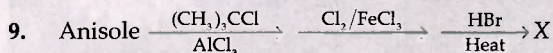
7. Photoelectric emission is observed from a surface for frequencies ν_1 and ν_2 of the incident radiations ($\nu_1 > \nu_2$). If the maximum K.E. of the photoelectrons in two cases are in the ratio 1 : K, then the threshold frequency ν_0 is given by

- $\frac{\nu_2 - \nu_1}{K - 1}$
- $\frac{K\nu_1 - \nu_2}{K - 1}$
- $\frac{K\nu_2 - \nu_1}{K - 1}$
- $\frac{\nu_2 - \nu_1}{K}$

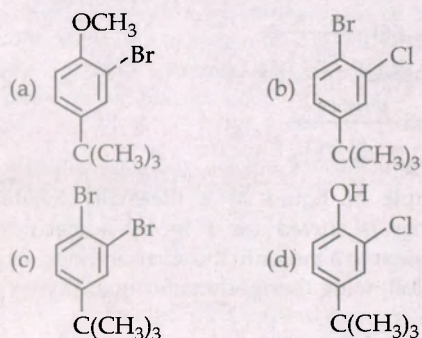
8. Correct R, S configuration of the following compound is



- (a) R at P and R at Q (b) R at P and S at Q
(c) S at P and R at Q (d) S at P and S at Q



The product X in the above series of reactions is



10. A white crystalline salt P reacts with dilute HCl to liberate a suffocating gas Q and also forms a yellow precipitate. The gas Q turns potassium dichromate acidified with dilute H_2SO_4 to a green coloured solution R. P, Q and R are respectively

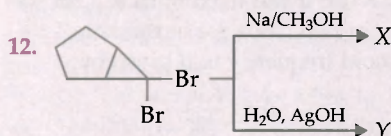
- (a) $\text{Na}_2\text{S}_2\text{O}_3$, SO_2 , $\text{Cr}_2(\text{SO}_4)_3$
(b) Na_2SO_3 , SO_2 , $\text{Cr}_2(\text{SO}_4)_3$
(c) Na_2SO_4 , SO_2 , $\text{Cr}_2(\text{SO}_4)_3$
(d) Na_2S , SO_2 , $\text{Cr}_2(\text{SO}_4)_3$

11. The electronic configurations of four elements are given below.

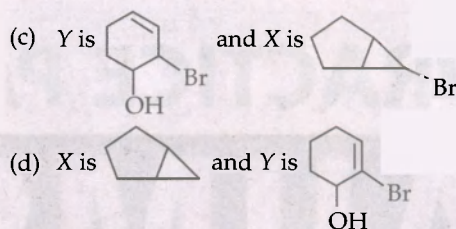
1. $2s^2 2p^5$ 2. $3s^2 3p^5$
3. $2s^2 2p^4$ 4. $3s^2 3p^4$

Arrange these elements in the correct order of the magnitude (without sign) of their electron affinity.

- (a) $1 < 2 < 4 < 3$ (b) $2 < 1 < 4 < 3$
(c) $1 < 3 < 4 < 2$ (d) $3 < 4 < 1 < 2$



- (a) X is and Y is
(b) X is and Y is



13. The salts of which pair are expected to have same colour in their freshly prepared aqueous solutions?

- (a) VOCl_2 , CuCl_2 (b) CuCl_2 , FeCl_2
(c) FeCl_2 , VOCl_2 (d) MnCl_2 , FeCl_2

14. When 2 g of a non-volatile hydrocarbon containing 94.4% carbon is dissolved in 100 g of benzene, the vapour pressure of benzene is lowered from 74.66 torr to 74.01 torr. What will be the molecular formula of the hydrocarbon?

- (a) C_7H_8 (b) C_8H_{16}
(c) $\text{C}_{14}\text{H}_{10}$ (d) C_{10}H_6

15. The reaction $2K + L \longrightarrow M + N$ goes to completion and follows the following rate law

$$-\frac{d}{dt}[K] = k[K]^2[L]$$

For this reaction the values of x and y in the following table are

Set	$[K]_0 \times 10^6$ (mol dm ⁻³)	$[L]_0 \times 10^6$ (mol dm ⁻³)	Half-life($t_{1/2}$) (s)
1	300	40	62.6
2	300	60	x
3	5	300	625
4	10	300	y

- (a) 62.6 and 625 (b) 62.6 and 312.5
(c) 31.3 and 625 (d) 31.3 and 312.5

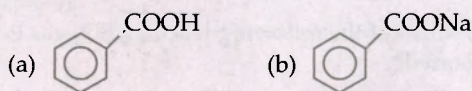
16. Pollutant of automobile exhausts that affects nervous system and produces mental diseases is

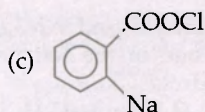
- (a) Lead (b) Mercury
(c) Nitric oxide (d) Sulphur dioxide

17. If Cl_2 gas is passed into aqueous solution of KI containing some CCl_4 and the mixture is shaken, then

- (a) copper layer becomes violet
(b) lower layer becomes violet
(c) homogeneous violet layer is formed
(d) None of the above

18. Toluene reacts with excess of Cl_2 in presence of sunlight to give a product which on hydrolysis followed by reaction with NaOH gives



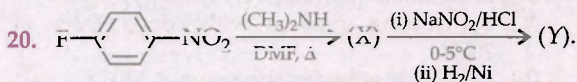


(d) None of the above.

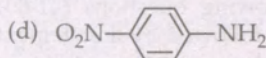
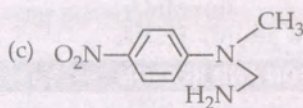
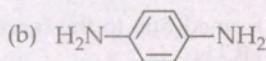
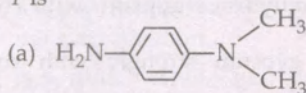
19. Which one of the following complexes is an outer orbital complex?

- (a) $[\text{Fe}(\text{CN})_6]^{4-}$ (b) $[\text{Mn}(\text{CN})_6]^{4-}$
(c) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (d) $[\text{Ni}(\text{NH}_3)_6]^{2+}$

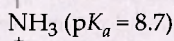
(Atomic numbers; Mn = 25, Fe = 26, Co = 27, Ni = 28)



Y is



21. Isoelectric point of given amino acid is,
 $\text{R}-\text{CH}_2-\text{CH}-\text{COOH}$ ($\text{pK}_b = 11.7$)



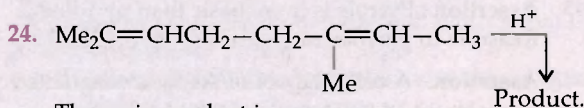
- (a) 6.4 (b) 5.5
(c) 11 (d) 3.2

22. The composition of a sample of wustite is $\text{Fe}_{0.93}\text{O}$. What is the percentage of iron present as Fe^{3+} ?

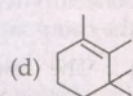
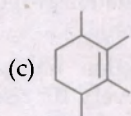
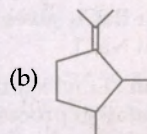
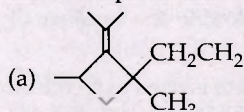
- (a) 15% (b) 25%
(c) 35% (d) 45%

23. What is the product of the reaction of H_2O_2 with Cl_2 ?

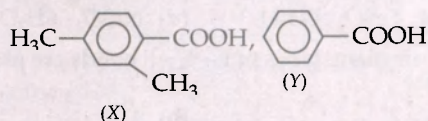
- (a) $\text{O} + \text{HOCl}$ (b) $\text{HCl} + \text{O}_2$
(c) $\text{H}_2\text{O} + \text{HCl}$ (d) $\text{HCl} + \text{H}_2$



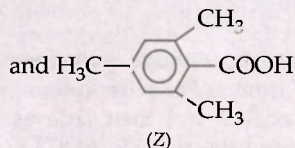
The main product is



25. Three acids are given:



(Y)



The correct order of ease of acid-catalysed esterification is

- (a) $X > Z > Y$ (b) $Y > X > Z$
(c) $Z > X > Y$ (d) $Y > Z > X$

26. Which one of the following statements is true?

- (a) Less is the critical temperature of a gas, greater is its adsorption.
(b) Higher is the critical temperature of a gas, greater is its adsorption.
(c) Greater is the van der Waals constant 'a' of a gas, less is its adsorption.
(d) A gas cannot be adsorbed above its critical temperature.

27. Heating an aqueous solution of aluminium chloride to dryness will give

- (a) $\text{Al}(\text{OH})\text{Cl}_2$ (b) Al_2O_3
(c) Al_2Cl_6 (d) AlCl_3

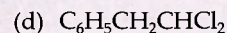
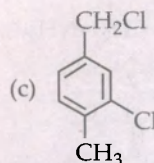
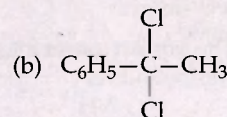
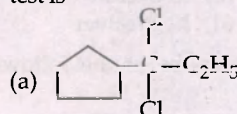
28. What will be the reduction potential of copper at $\text{pH} = 14$ if K_{sp} of $\text{Cu}(\text{OH})_2$ is 1.0×10^{-19} and $E_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$?

- (a) +0.34 V (b) -0.22 V
(c) -0.33 V (d) -0.34 V

29. The density of a mixture of N_2 and O_2 at NTP is 1.3 g L^{-1} . Calculate the partial pressure of O_2 .

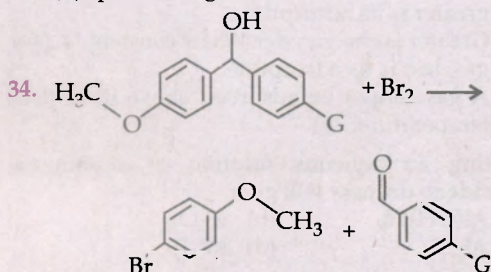
- (a) 2.8 atm (b) 0.25 atm
(c) 0.28 atm (d) 1.28 atm

30. Structure of $\text{C}_8\text{H}_8\text{Cl}_2$, which on aqueous alkali hydrolysis gives a product which does not give positive iodoform test, but gives silver mirror test is



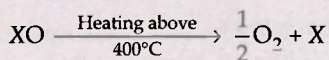
31. Amongst the following, the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by

- (a) $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ (b) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
(c) $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ (d) $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
32. How many types of F—S—F bonds are present in SF_4 ?
(a) 2 (b) 4
(c) 3 (d) 5
33. When a vapour at atmospheric pressure was gradually heated from 298 K; its colour was found to deepen at first and then fade as the temperature was raised above 433 K. At 873 K, the vapour becomes almost colourless, but its colour deepened when the pressure was raised keeping the temperature constant. The vapour was
(a) the bromine
(b) A mixture of nitrogen dioxide and dinitrogen tetroxide
(c) pure dinitrogen tetroxide
(d) pure nitrogen dioxide.



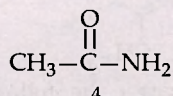
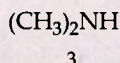
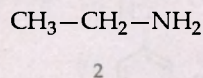
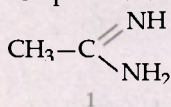
The rate of reaction is moderately affected by the nature of G. Choose the correct decreasing rate of reaction with various substituents as G.

- (a) $-\text{NO}_2 > -\text{Br} > -\text{H} > -\text{CH}_3 > -\text{OCH}_3$
(b) $-\text{OCH}_3 > -\text{CH}_3 > -\text{H} > -\text{Br} > -\text{NO}_2$
(c) $-\text{OCH}_3 > -\text{Br} > -\text{CH}_3 > -\text{H} > -\text{NO}_2$
(d) $-\text{NO}_2 > -\text{OCH}_3 > -\text{Br} > -\text{H} > -\text{CH}_3$
35. $\text{MCl}_2 + \text{XCl}_2 (\text{excess}) \rightarrow \text{MCl}_4 + \text{X} \downarrow$



An ore of X could be

- (a) cinnabar (b) malachite
(c) siderite (d) horn silver.
36. The correct order of basicities of the following compounds is



- (a) $2 > 1 > 3 > 4$ (b) $1 > 3 > 2 > 4$
(c) $3 > 1 > 2 > 4$ (d) $1 > 2 > 3 > 4$

37. Aqueous 10% NaHCO_3 solution is used as reagent for identifying X. Which one of the following compounds yields X on hydrolysis?
(a) $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ (b) $\text{C}_2\text{H}_5-\text{O}-\text{C}_2\text{H}_5$
(c) CH_3CHO (d) $\text{CH}_3\text{CH}_2\text{OH}$
38. The number of α -particles emitted per second by 1 g of ^{226}Ra is 3.7×10^{10} . The decay constant is
(a) $1.39 \times 10^{-11} \text{ s}^{-1}$ (b) $13.9 \times 10^{-11} \text{ s}^{-1}$
(c) $13.9 \times 10^{-10} \text{ s}^{-1}$ (d) $13.9 \times 10^{-10} \text{ s}^{-1}$
39. SO_2 is obtained quantitatively from gypsum
(a) by treating gypsum with conc. HNO_3 at 700°C
(b) by heating anhydrous gypsum at 1200°C
(c) by heating anhydrous gypsum with conc. HCl at 1200°C
(d) by heating gypsum strongly with conc. H_2SO_4 .
40. One of the products formed due to the reaction between KMnO_4 and HCl is
(a) red liquid (b) MnO_2
(c) greenish yellow gas (d) HClO_4 .

ASSERTION AND REASON

Directions : In the following questions (41-60), a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

41. **Assertion :** NO_2 turns acidic KI -starch paper blue.

Reason : NO_2 turn I^- into I_2 .

42. **Assertion :** Cu^+ ion is colourless.

Reason : Four water molecules are coordinated to Cu^+ ion.

43. **Assertion :** Pyrrole is more basic than pyridine.

Reason : In pyrrole, nitrogen is sp^3 hybridized.

44. **Assertion :** A colloidal sol of As_2S_3 is coagulated faster by 0.1 M BaCl_2 than by 0.1 M NaCl .

Reason : BaCl_2 gives double the number of Cl^- ions than NaCl .

45. **Assertion :** Ethyl xanthate is used as a collector in froth floatation process.

Reason : Collectors depress the floatation property of one of the components of the ore.

46. **Assertion :** The rate of a reaction normally increases by a factor of 2 or 3 for every 10° rise in temperature.

Reason : Increase in temperature increases the number of collisions.

47. **Assertion :** Li^+ ion has the lowest mobility in aqueous solution.

Reason : Lithium has higher ionization enthalpy.

48. **Assertion :** The electron gain enthalpy of N is +ve while that of P is -ve.

Reason : This is due to the smaller atomic size of N in which there is a considerable electron-electron repulsion and hence the additional electron is not accepted easily.

49. **Assertion :** Aniline on treatment with CS_2 ; HgCl_2 do not give mustard oil odour.

Reason : $\text{R}-\text{NCS}$, alkylisothiocyanate do not have mustard oil odour.

50. **Assertion :** Thiophene present in commercial benzene as an impurity can be removed by shaking the mixture with cold concentrated H_2SO_4 .

Reason : Thiophene is a heterocyclic aromatic compound.

51. **Assertion :** Dimethylamine has repulsive interaction with OH^- ion in the solution.

Reason : The ionisation constant of dimethylamine gets decreased in the alkaline NaOH solution.

52. **Assertion :** Concentrated aqueous solution of CuCl_2 is green in colour.

Reason : The solution contains two complex ions i.e., $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ and $[\text{CuCl}_4]^{2-}$ in equilibrium.

53. **Assertion :** In a galvanic cell : $\text{Zn} | \text{Zn}^{2+} || \text{Cu}^{2+} | \text{Cu}$ after complete discharging, the equilibrium gets established.

Reason : In galvanic cell, $\text{Zn} | \text{Zn}^{2+} || \text{Cu}^{2+} | \text{Cu}$ after complete discharging (Zn^{2+}) becomes equal to (Cu^{2+}).

54. **Assertion :** RCOCl , $(\text{RCO})_2\text{O}$ and RCOOR' all react with Grignard reagent to form 3° alcohols.

Reason : RCOCl reacts with R_2Cd to form ketones but $(\text{RCO})_2\text{O}$ and RCOOR' do not react at all.

55. **Assertion :** Benzaldehyde undergoes aldol condensation.

Reason : Aldehydes that do not have α -hydrogen undergo aldol condensation.

56. **Assertion :** F^- ion is a weak ligand and forms outer orbital complex.

Reason : F^- ion cannot force the electrons of d_{z^2} and $d_{x^2-y^2}$ orbitals of the inner shell to occupy d_{xy} , d_{yz} and d_{zx} -orbitals of the same shell.

57. **Assertion :** $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ always contains Fe^{3+} ions.

Reason : This is due to aerial oxidation of Fe^{2+} ions.

58. **Assertion :** A spectral line will be observed for a $2p_x - 2p_y$ transition.

Reason : The energy is released in the form of wave of light when electron drops from $2p_x$ to $2p_y$ orbital.

59. **Assertion :** Compressibility factor (Z) for non-ideal gases is always greater than 1.

Reason : Non-ideal gases always exert higher pressure than expected.

60. **Assertion :** Saline hydrides are non-volatile, non-conducting and crystalline solids.

Reason : Saline hydrides are compounds of hydrogen with most of the p -block elements.

SOLUTIONS

1. (a): Let x mL of 3 M and $(1000 - x)$ mL of 1 M HCl are mixed.

$$M_1V_1 + M_2V_2 = M_3V_3$$

$$3x + 1(1000 - x) = 1.2 \times 1000$$

$$\text{or } 3x + 1000 - x = 1200$$

$$\text{or } x = 100 \text{ mL}$$

Thus, 100 mL of 3 M and 900 mL of 1 M HCl should be mixed.

2. (a): Structure (a) is least stable because the same charges (positive charges) are present at nearest positions.

3. (a): $K_{eq} = Ae^{-\Delta H^\circ/RT}$

$$\ln K_{eq} = \ln A - \frac{\Delta H^\circ}{RT}$$

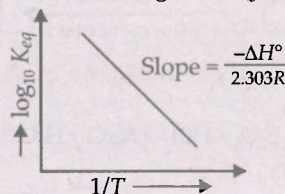
$$2.303 \log K_{eq} = 2.303 \log A - \frac{\Delta H^\circ}{RT}$$

$$\log_{10} K_{eq} = \log_{10} A - \frac{\Delta H^\circ}{2.303R} \cdot \frac{1}{T}$$

A graph between $\log_{10} K_{eq}$ and $\frac{1}{T}$ will give straight

line slope = $-\frac{\Delta H^\circ}{2.303}$ and intercept = $\log_{10} A$

This is equation of a straight line ($y = mx + c$).



4. (d): $\text{Na}_2\text{S} + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{S}$

5. (d): For a thermally insulated container, $\Delta q = 0$. But work (W), change in internal energy (ΔE) and change in enthalpy (ΔH) are non-zero.

6. (b): When the combination is Fe^{2+} and NO , there will be 5 unpaired electrons in the complex (4 in Fe^{2+} and 1 in NO) and when the combination is Fe^+ and NO^+ , there will be only 3 unpaired electrons

which can be differentiated by measuring the magnetic moments.

7. (b): $KE_1 = h\nu_1 - h\nu_0$, $KE_2 = h\nu_2 - h\nu_0$

$$\frac{KE}{KE_2} = \frac{1}{K} \text{ or } \frac{h(\nu_1 - \nu_0)}{h(\nu_2 - \nu_0)} = \frac{1}{K}$$

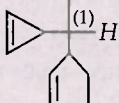
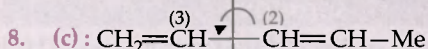
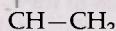
or $K\nu_1 - K\nu_0 = \nu_2 - \nu_0$

or $K\nu_1 - \nu_2 = K\nu_0 - \nu_0$

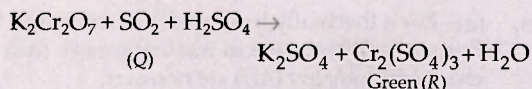
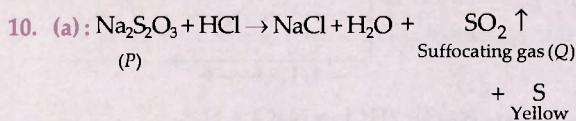
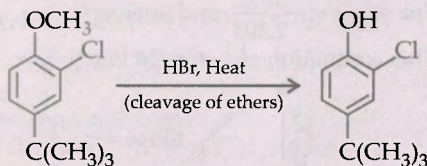
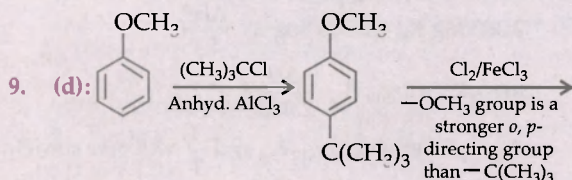
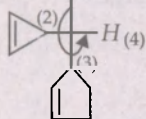
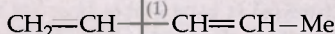
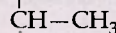
$$K\nu_1 - \nu_2 = \nu_0 (K - 1)$$

$$\nu_0 = \frac{K\nu_1 - \nu_2}{K - 1}$$

(4) Me

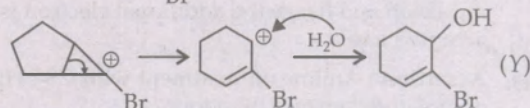
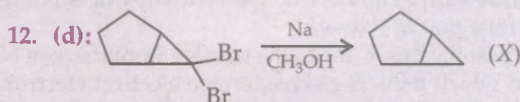


Me



11. (d): Elements with electronic configurations 1 and 3 belong to second period and groups 17 and 16 respectively whereas the elements with electronic configurations 2 and 4 belong to third period

and groups 17 and 16 respectively. Thus, the least negative EA is of 3 due to electron-electron repulsion in the compact 2p-orbital. The more negative EA is of 4, then 1 (halogen) and most -ve is of 2 (halogen). Thus, the correct order is $3 < 4 < 1 < 2$.



13. (a): In VOCl_2 , V^{4+} has d^1 configuration. In CuCl_2 , Cu^{2+} has d^9 configuration. Both have 1 unpaired electron, so these have same colour in aqueous solution.

14. (c): Raoult's law = $-\frac{\Delta P}{P^\circ} = x_2$

$$\Delta P = (74.01 - 74.66) \text{ torr}$$

$$P^\circ = 74.66 \text{ torr}$$

If M is the molar mass of hydrocarbon, then

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{2/M}{(100/78) + (2/M)}$$

Hence, $\frac{74.66 - 74.01}{74.66} = \frac{2/M}{(100/78) + (2/M)}$

$$M = 177.6 \text{ g mol}^{-1}$$

$$m_C : m_H :: 94.4 : 5.6$$

Thus atomic ratio is $N_C : N_H :: \frac{94.4}{12} : \frac{5.6}{1}$

$$\Rightarrow 7.87 : 5.6 \Rightarrow 1.4 : 1 \Rightarrow 7 : 5$$

Hence empirical formula is C_7H_5

Molar empirical mass = 89 g mol^{-1}

No. of C_7H_5 units = $\frac{\text{molar mass}}{\text{empirical mass}} = \frac{177.6}{89} = 2$

Hence, molecular formula = $\text{C}_{14}\text{H}_{10}$

15. (b): In more than one reactant system, the half-life time ($t_{1/2}$) is the time for half of the reactant present in small amount.

For set (1) and (2), L is in small amount and according to rate law, the reaction is of first order w.r.t. L. So in these sets the half-life is independent of initial concentration and so the $t_{1/2}$ for set(2) will be same as that for set (1) i.e. $x = 62.6 \text{ s}$. In set (3) and (4), K is present in small quantity and $t_{1/2}$ will depend on [K]. According to rate law expression the order w.r.t. K is 2.

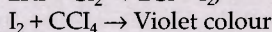
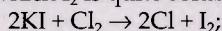
$$\therefore t_{1/2} = \frac{1}{k \cdot a} = \frac{1}{k[A_0]^2} \text{ or } \frac{(t_{1/2})_3}{(t_{1/2})_4} = \frac{[A_0]_4}{[A_0]_3}$$

$$\text{or } \frac{625}{(t_{1/2})_4} = \frac{10}{5} \text{ or } 2$$

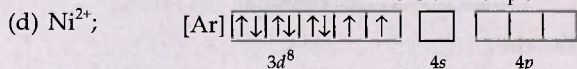
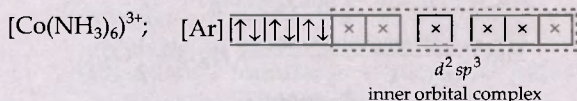
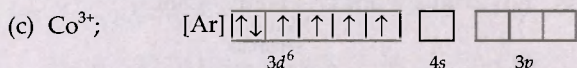
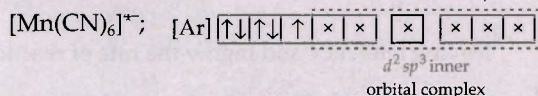
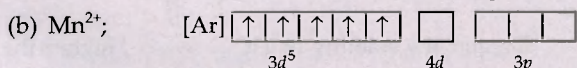
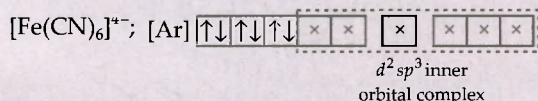
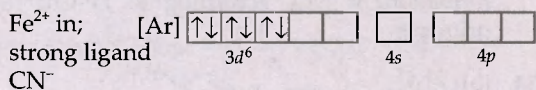
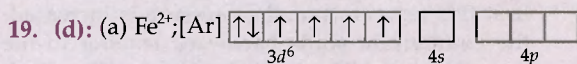
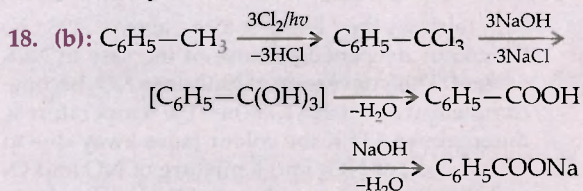
$$\therefore (t_{1/2})_4 = \frac{625}{2} = 312.5 \text{ s i.e., } y = 312.5$$

16. (a): Lead coming from automobile exhausts produces mental diseases.

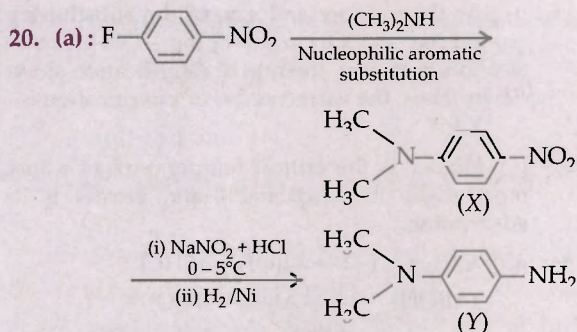
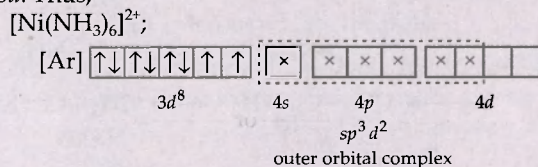
17. (b): When chlorine gas is bubbled into an aq. solution of KI, some of the I^- ions are oxidized to I_2 . The I_2 molecules combine with I^- ions to form brown I_3^- , the aq. solution is above a larger of CCl_4 in which I_2 is quite soluble.



(lower layer because CCl_4 is heavier than water)



In this case also NH_3 is a strong ligand but electrons remain unpaired since only one orbital is left vacant in $3d$. Thus,



21. (b): At isoelectric point

$$\text{pI} = \frac{1}{2} [\text{pK}_a + \text{pK}_b] = \frac{1}{2} [8.7 + (14 - 11.7)]$$

$$= \frac{1}{2} [8.7 + 2.3] = \frac{11}{2} = 5.5$$

22. (a): Let, no. of O^{2-} ions in $\text{Fe}_{0.93}\text{O} = 100$

\therefore Total no. of Fe^{2+} and Fe^{3+} ions = 93

Let no. of Fe^{2+} ions in the sample = x and
 no. of Fe^{3+} ions in the sample = y

$$\therefore x + y = 93 \quad \dots(i)$$

Total -ve charge carried by 100 O^{2-} ions = 200

Total +ve charge carried by x Fe^{2+} ions = $2x$

Total charge carried by y Fe^{3+} ions = $3y$

Thus, $2x + 3y = 200 \quad \dots(ii)$

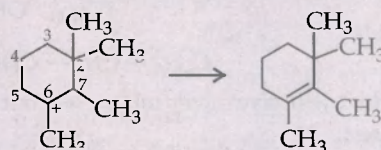
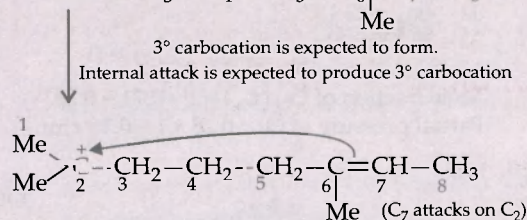
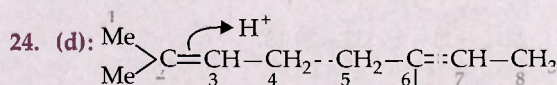
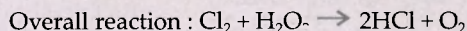
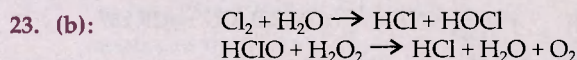
Solving (i) and (ii), we get $x = 79$, and $y = 14$

\therefore No. of Fe^{2+} ions, $x = 79$, and

\therefore No. of Fe^{3+} ions, $y = 14$

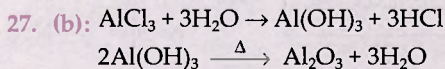
\therefore % of iron present as Fe^{3+}

$$= \frac{14}{79 + 14} \times 100 = 15.05\%$$



25. (b): As the number and size of the substituents around the $-\text{COOH}$ group or the $-\text{OH}$ group in alcohols increases, the rate of esterification slows down. Thus, the correct order of esterification is $Y > X > Z$.

26. (b): Higher is the critical temperature of a gas, more easily it is liquefiable and greater is its adsorption.



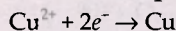
28. (b): $\text{pH} = 14, \therefore \text{pOH} = 0$

$$[\text{OH}^-] = 1\text{M}$$

$$K_{sp} = [\text{Cu}^{2+}][\text{OH}^-]^2$$

$$[\text{Cu}^{2+}] = \frac{K_{sp}}{[\text{OH}^-]^2} = \frac{1 \times 10^{-19}}{1}$$

$$= 1 \times 10^{-19}$$



$$E_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Cu}^{2+}/\text{Cu}} = \frac{0.0591}{n} \log \frac{1}{[\text{Cu}^{2+}]}$$

$$= 0.34 - \frac{0.0591}{2} \log 10^{19}$$

$$= 0.34 - \frac{0.0591 \times 19}{2}$$

$$= -0.22 \text{ V}$$

29. (c): Let x_{N_2} and x_{O_2} mole fraction of N_2 and O_2 be present in the mixture respectively. Average molecular mass of mixture (M) from general gas equation.

$$M = \frac{D}{P} \times RT = \frac{1.3}{1} \times 0.0821 \times 273 = 29.137$$

$$x_{\text{N}_2} M_{\text{N}_2} + x_{\text{O}_2} M_{\text{O}_2} = 29.137$$

$$x_{\text{N}_2} \times 28 + x_{\text{O}_2} \times 32 = 29.137$$

$$\text{Since } x_{\text{O}_2} = 1 - x_{\text{N}_2}$$

$$28x_{\text{N}_2} + (1 - x_{\text{N}_2})32 = 29.137$$

$$28x_{\text{N}_2} + 32 - 32x_{\text{N}_2} = 29.137$$

$$32 - 4x_{\text{N}_2} = 29.137$$

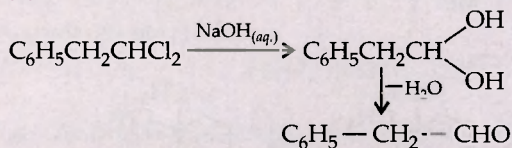
$$32 - 29.137 = 4x_{\text{N}_2}$$

$$\text{Mole fraction of } \text{N}_2, (x_{\text{N}_2}) = 0.71$$

$$\text{Mole fraction of } \text{O}_2, (x_{\text{O}_2}) = 1 - 0.71 = 0.28$$

$$\text{Partial pressure of } \text{O}_2 = 0.28 \times 1 = 0.28 \text{ atm}$$

30. (d):

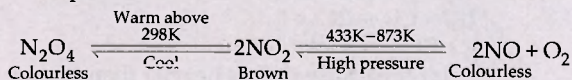


Final product will give silver mirror test but not iodoform test.

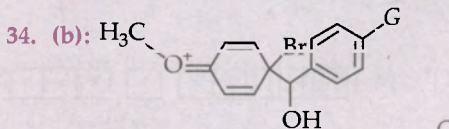
31. (b): Mn^{2+} in $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ has d^5 configuration (five unpaired electrons); Cu^{2+} in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ has d^9 configuration (one unpaired electron); Fe^{2+} in $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ has d_6 configuration (four unpaired electrons) and Ni^{2+} in $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ has d^8 configuration (two unpaired electrons). Thus $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ has lowest degree of paramagnetism.

32. (a): Two axial and two equatorial bonds.

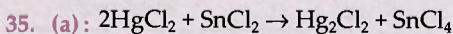
33. (b): NO_2 and N_2O_4 are present in equilibrium as represented below:



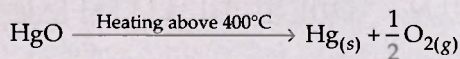
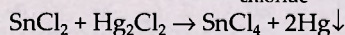
On raising the temperature above 298 K, the colour deepened because of increase in NO_2 content. This conversion of N_2O_4 into NO_2 become complete at about 413 K. When the temperature is raised above 433 K the colour fades away due to dissociation of NO_2 into a mixture of NO and O_2 and this is complete at about 873 K (colourless). If at this temperature, the pressure is increased, the equilibrium shifts backward leading to the formation of NO_2 according to Le-Chatelier's principle.



Greater the stability of HC^+ , higher the leaving tendency and higher the rate of reaction.

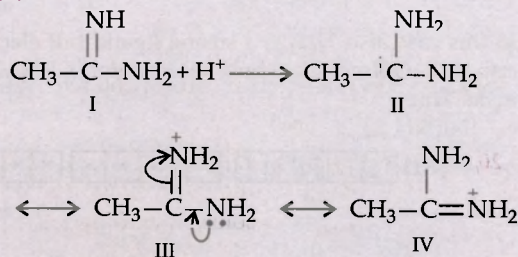


Mercurous chloride



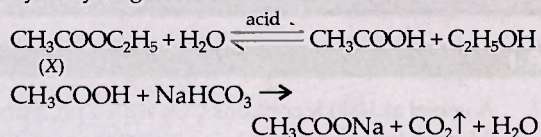
Hence, ore is HgS , cinnabar.

36. (b):



The conjugate acid (III) obtained by addition of a proton to (I) is stabilized by two equivalent resonance structures and hence compound (I) is the most basic. Further 2° amines are more basic than 1° amines while amides are least basic due to delocalization of lone pair of electrons of N over the C=O group. Thus, the order : 1 > 3 > 2 > 4.

37. (a): Acetic acid liberates CO₂ gas on reaction with 10% NaHCO₃ solution. Ethyl acetate on hydrolysis gives acetic acid.

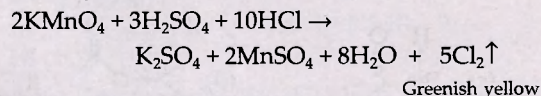


38. (a): $\lambda = \frac{\text{No. of atoms disintegrating per second}}{\text{Total number of atoms present}}$

$$\begin{aligned} \text{or } \lambda &= \frac{3.7 \times 10^{10}}{6.02 \times 10^{23}} = \frac{226 \times 3.7 \times 10^{10}}{6.02 \times 10^{23}} \\ &= \frac{226}{1} \\ &= 1.39 \times 10^{-11} \text{ s}^{-1} \end{aligned}$$

39. (b): $\text{CaSO}_4 \xrightarrow{1200^\circ\text{C}} 2\text{CaO} + 2\text{SO}_2 + \text{O}_2$
Anhydrous

40. (c): A greenish yellow gas is formed.



41. (a): NO₂ is an acid radical and oxidizing reagent, it oxidises I⁻ into I₂.



42. (c): Cu⁺ ion has 3d¹⁰ outer electronic configuration where no d-d transition is possible.

43. (d): Pyridine is more basic than pyrrole. In pyridine, the lone pair of electrons on N is available for protonation but in pyrrole they are contributed towards aromatic sextet formation. The N-atom in pyrrole is sp² hybridised.

44. (b): As₂S₃ being negatively charged, is coagulated faster by Ba²⁺ ions than by Na⁺ ions.

45. (c): Collectors attach themselves by polar groups to grains of ores which then become water repellent and pass on into the froth.

46. (b): With increase in temperature by 10°C, the fraction of molecules possessing energy equal to or greater than threshold value becomes 2 or 3 times.

47. (b): Because of extensive hydration, the effective size of Li⁺ is the largest in aqueous solution.

48. (a): N required extra energy in order to add an extra electron.

49. (d): Aniline gives Hofmann's mustard oil reaction.

50. (b): On shaking with concentrated H₂SO₄ thiophene being more reactive undergoes sulphonation and the thiophene-2-sulphonic acid thus formed dissolves in concentrated H₂SO₄.

51. (c): $(\text{CH}_3)_2\text{NH} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_2\text{NH}_2^+ + \text{OH}^-$

Addition of OH⁻ increases the common ion, OH⁻ concentration, shifts reaction backward respective [(CH₃)₂NH] gets increased, but ionisation constant remains constant.

Second statement is correct as these two are parts of equilibrium mixture.

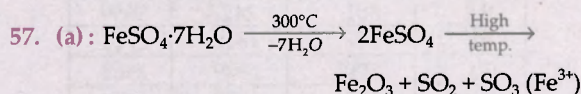
52. (a)

53. (c): Complete discharging of cell suggests equal potential at the cathode and anode.

54. (b): RCOCl, (RCO)₂O and RCOOR' all add two molecules of Grignard reagent to give 3° alcohols.

55. (d): Aldehydes having a methyl or methylene group in the α-position or more correctly having atleast one hydrogen atom in the α-position undergo dimerisation in presence of a base at low temperature to form β-hydroxy aldehydes called aldols.

56. (a)



58. (d): 2p_x and 2p_y orbitals are degenerate orbitals, i.e., they are of equal energy and hence no possibility of transition of electron.

59. (d): Z can be greater than 1 or less than 1. Non-ideal gases exert lower pressure than expected due to backward pull by other molecules.

60. (c): Saline or ionic hydrides are compounds of hydrogen with most of the s-block metals. However, with p-block metals hydrogen forms molecular or covalent hydrides.

PRACTICE PAPER 2 Q 13

JEE Advanced

Exam on
2nd June
2013

PAPER-I

SECTION-I

Straight Objective Type

This section contains 10 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- The temperature of blast furnace to produce iron from its ore Fe_2O_3 varies from 500°C at the top of the furnace to about 1900°C at the bottom of the furnace. The reaction between the ore Fe_2O_3 and CO at the lowest temperature ($\sim 500^\circ\text{C}$) is
 (a) $3\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2$
 (b) $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$
 (c) $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{FeO} + 3\text{CO}_2$
 (d) $\text{Fe}_2\text{O}_3 + \text{CO} + \text{CaCO}_3 \rightarrow \text{Fe}_2\text{O}_3 + \text{CO} + \text{CO}_2 + \text{CaO}$
- In general, the first ionisation energy decreases in a regular way on descending the main groups. A departure from this trend is observed in group 13 as follows :

Element	Ionisation energy (in kJ mol^{-1})		
	1st	2nd	3rd
B	801	2427	3659
Al	577	1816	2744
Ga	579	1979	2962
In	558	1820	2704

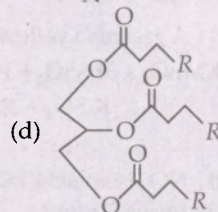
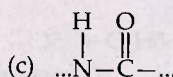
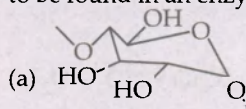
Gallium has higher ionisation energy in comparison to Al because

- gallium is harder than aluminium
- gallium is preceded by ten transition elements, where $3d$ shell is being filled which makes Ga larger than it would be
- gallium is preceded by ten transition elements, where $3d$ shell is being filled which makes Ga smaller than it would be
- effective nuclear charge for Ga is much higher than Al.

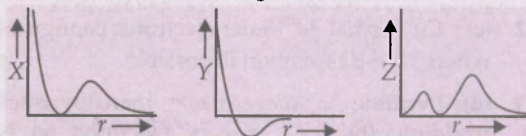
- A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm . Some of the CO_2 is converted into CO on the addition of graphite. The value of K if the total pressure at equilibrium is 0.8 atm is

- 1.8 atm
- 3 atm
- 0.3 atm
- 0.18 atm

- Which of the following chemical unit is certainly to be found in an enzyme?



- Plots for $2s$ -orbital are given below.



X, Y and Z are respectively

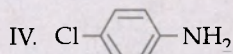
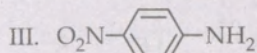
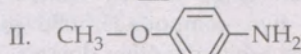
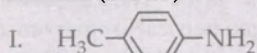
- Ψ , Ψ^2 and $4\pi r^2 \Psi^2$
- Ψ^2 , Ψ and $4\pi r^2 \Psi^2$
- $4\pi r^2 \Psi^2$, Ψ^2 and Ψ
- Ψ^2 , $4\pi r^2 \Psi^2$ and Ψ

- During the transformation of ${}^a\text{X}$ to ${}^b\text{Y}$ by α and β -decay, the number of β -particles emitted are

- $\frac{a-b}{4}$
- $d + \frac{a-b}{2} + c$
- $d + \left(\frac{a-b}{2}\right) - c$
- $2c - d + a - b$

- Which of the following sets of species does not follow octet rule?

- (a) CO , PCl_5 , PCl_3 , AlCl_3
 (b) CO , B_2H_6 , NH_3 , H_2O
 (c) AlCl_3 , BF_3 , PCl_5 , SF_6
 (d) H_2O , NH_3 , CO_2 , AlCl_3
8. Bottles containing $\text{C}_6\text{H}_5\text{I}$ and $\text{C}_6\text{H}_5\text{CH}_2\text{I}$ lost their original labels. They were labelled A and B for testing. A and B were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and some AgNO_3 solution was added. Solution B gave a yellow precipitate. Which one of the following statements is true for the experiment?
- (a) Addition of HNO_3 was unnecessary
 (b) A was $\text{C}_6\text{H}_5\text{I}$
 (c) A was $\text{C}_6\text{H}_5\text{CH}_2\text{I}$
 (d) B was $\text{C}_6\text{H}_5\text{I}$
9. The basic characters of the given substituted anilines (I to IV)



are such that

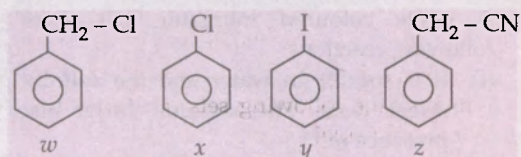
- (a) $\text{I} > \text{II} > \text{IV} > \text{III}$ (b) $\text{I} > \text{II} > \text{III} > \text{IV}$
 (c) $\text{II} > \text{I} > \text{III} > \text{IV}$ (d) $\text{II} > \text{I} > \text{IV} > \text{III}$
10. A 1.5276 g sample of CdCl_2 was converted to metallic cadmium and cadmium-free products by an electrolytic process. The weight of the metallic cadmium was 0.9367g. If the atomic weight of chlorine is taken as 35.453, what must be the atomic weight of Cd from this experiment?
- (a) 112.41 (b) 113.1
 (c) 112.20 (d) 112.61

SECTION - II

Multiple Correct Answer Type

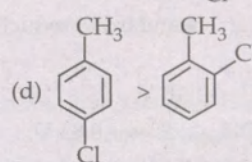
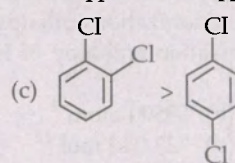
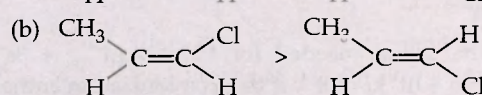
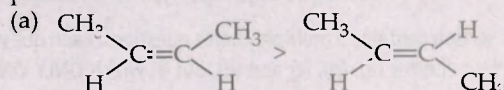
This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

11. Four compounds are noted below. Arrange them in order of decreasing reactivity towards nitration.



- (a) $x > z > y > w$ (b) $x > w > y > z$
 (c) $y > x > w > z$ (d) $w > z > y > x$

12. A complex is prepared by mixing CoCl_3 and NH_3 . 0.1 M solution of the complex was found to freeze at -0.372°C . The formula of the complex is
- (a) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (b) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
 (c) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ (d) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
13. $(\text{MnSO}_4 + \text{H}_2\text{O}_2)$ solution is used to detect NH_3 gas, which produces a black ppt. of $\text{MnO}(\text{OH})_2$. The same observation may be obtained when a solution A is added to the above solution. Then A may be
- (a) KOH (b) NaOH
 (c) $\text{Ca}(\text{OH})_2$ (d) only (a) and (b).
14. Which order is/are correct regarding boiling point?



15. The correct characteristics of lyophilic and lyophobic colloid(s) is/are
- (a) Lyophilic sols are highly hydrated while lyophobic sols are not.
 (b) Lyophilic sols have lower surface tension and viscosity than that of the dispersion medium.
 (c) Lyophobic sols can be easily coagulated but lyophilic sols are not.
 (d) Gold sol is irreversible sol because gold cannot be obtained back.

SECTION - III

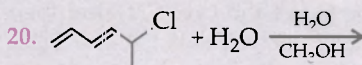
Integer Answer Type

This section contains 5 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

16. The difference between number of lone pairs and number of S—S bonds in S_8 molecule is

17. The rate of a reaction starting with initial concentrations $2 \times 10^{-3} \text{ M}$ and $1 \times 10^{-3} \text{ M}$ are equal to $2.40 \times 10^{-4} \text{ M s}^{-1}$ and $0.60 \times 10^{-4} \text{ M s}^{-1}$ respectively. The order of reaction is,
18. The number of possible isomers of an octahedral complex, $[\text{Co}(\text{C}_2\text{O}_4)_2(\text{NH}_3)_2]^-$ is
19. A solution containing 0.1 g of a non-volatile organic substance P (molecular mass 100) in 100 g of benzene raises the boiling point of benzene by 0.2°C , while a solution containing

0.1 g of another non-volatile substance Q in the same amount of benzene raises the boiling point of benzene by 0.4°C . The ratio of molecular masses of P and Q is $x : 1$ where x is



In this reaction we get ... types of substituted alcohols (stereoisomers not considered)

- (a) one (b) two
(c) three (d) four

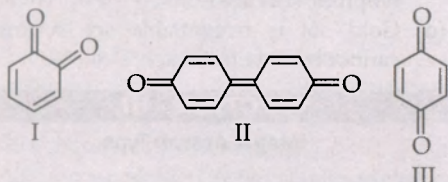
PAPER-II

SECTION-I

Straight Objective Type

This section contains 8 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

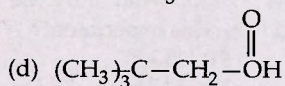
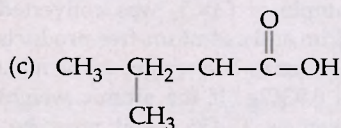
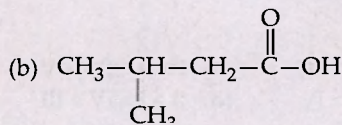
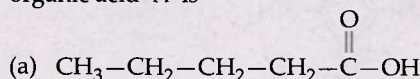
21. The energy needed for $\text{Li}_{(\text{g})} \rightarrow \text{Li}^{3+}_{(\text{g})} + 3e^-$ is $1.96 \times 10^4 \text{ kJ mol}^{-1}$, if the first ionization enthalpy of Li is 520 kJ mol^{-1} , second ionization enthalpy of Li is approximately (Ionization enthalpy of H is $2.18 \times 10^{-18} \text{ J/atom}$)
- (a) 5950 kJ mol^{-1} (b) 5950 J atom^{-1}
(c) 7270 kJ mol^{-1} (d) $727.0 \text{ kJ mol}^{-1}$
22. Given the following standard reduction potentials :
- $\text{Mn}^{+2}_{(\text{aq})} + 2e^- \rightarrow \text{Mn}_{(\text{s})}; E^\circ = -1.18 \text{ V}$
 $2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_{2(\text{g})} + 2\text{OH}^-_{(\text{aq})}; E^\circ = -0.83 \text{ V}$
 $\text{I}_2 + 2e^- \rightarrow 2\text{I}^-_{(\text{aq})}; E^\circ = +0.53 \text{ V}$
 $\text{O}_{2(\text{g})} + 4\text{H}^+_{(\text{aq})} + 4e^- \rightarrow 2\text{H}_2\text{O}; E^\circ = +1.23 \text{ V}$
 Electrolysis of an aqueous solution of MnI_2 would give
- (a) H_2, I_2 (b) H_2, O_2
(c) Mn, O_2 (d) Mn, I_2
23. Consider the following conjugated diketone compounds.



Which of the following is the correct decreasing order of E° values?

- (a) $\text{I} > \text{II} > \text{III}$ (b) $\text{III} > \text{II} > \text{I}$
(c) $\text{I} > \text{III} > \text{II}$ (d) $\text{II} > \text{I} > \text{III}$

24. An organic acid $A(\text{C}_5\text{H}_{10}\text{O}_2)$ reacts with Br_2 in presence of phosphorus to produce a resolvable compound, which on dehydrobromination gives an unsaturated acid. The unsaturated acid does not show geometrical isomerism and on decarboxylation gives alkene. Alkene on ozonolysis gives two compounds, one gives positive Schiff's test while the other doesn't. The organic acid 'A' is



25. The composition of the equilibrium mixture for the equilibrium $\text{Cl}_2 \rightleftharpoons 2\text{Cl}$ at 1400 K may be determined by the rate of diffusion of mixture through a pin hole. It is found that at 1400 K, the mixture diffuses 1.16 times as fast as krypton diffuses under the same conditions. Find the degree of dissociation of Cl_2 equilibrium.

- (a) 0.116 (b) 0.1374
(c) 1.374 (d) 0.980

26. A white coloured inorganic salt gives the following reactions:

- (i) It is soluble in water and the solution has sweet taste. The solution turns black in presence of H_2S .

- (ii) The salt when heated gives acetone and a yellow coloured residue which is used in paints.
 (iii) The solution of the salt gives a white precipitate with dilute HCl which is soluble in hot water.

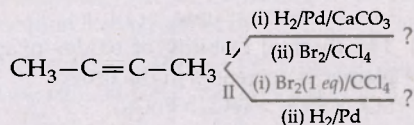
The inorganic salt is

- (a) $\text{Ca}(\text{CH}_3\text{COO})_2$ (b) $\text{Zn}(\text{CH}_3\text{COO})_2$
 (c) $\text{Pb}(\text{CH}_3\text{COO})_2$ (d) $\text{Ba}(\text{CH}_3\text{COO})_2$

27. NaCN is sometimes added in the Froth floatation process as a depressant when ZnS and PbS minerals are extracted because

- (a) NaCN causes reduction by precipitation
 (b) PbS forms soluble complex $\text{Na}_2[\text{Pb}(\text{CN})_4]$ while ZnS forms froth
 (c) $\text{Pb}(\text{CN})_2$ is precipitated while no effect on ZnS
 (d) ZnS forms soluble complex, $\text{Na}_2[\text{Zn}(\text{CN})_4]$ while PbS forms froth.

28. The product of the following I and II sequence are related as



- (a) diastereomers (b) identical
 (c) enantiomers (d) geometrical isomers.

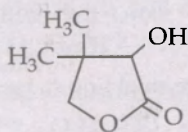
SECTION - II

Paragraph Type

This section contains 6 multiple choice questions relating to three paragraphs with two questions on each paragraph. Each question has four choices (a), (b), (c) and (d) out of which ONLY ONE is correct.

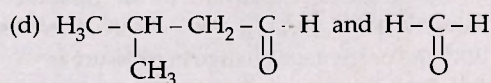
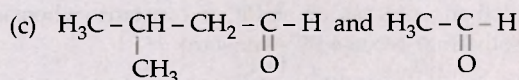
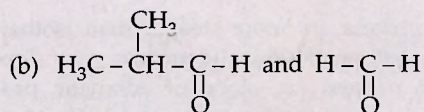
Paragraph for Questions 29 and 30

Two aliphatic aldehydes *P* and *Q* react in the presence of aqueous K_2CO_3 to give compound *R*, which upon treatment with HCN provides compound *S*. On acidification and heating *S* gives the product shown below:

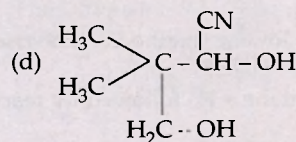
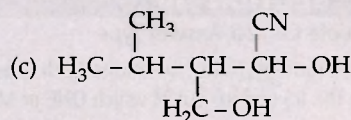
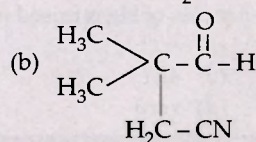
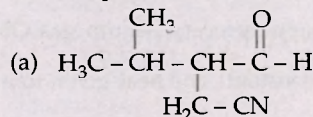


29. The compound *P* and *Q* respectively are

- (a) $\text{H}_3\text{C}-\text{CH}(\text{CH}_3)-\text{C}(=\text{O})-\text{H}$ and $\text{H}_3\text{C}-\text{C}(=\text{O})-\text{H}$



30. The compound *S* is



Paragraph for Questions 31 and 32

Fluorine, the first member of group 17, differs from the other members of the group in many respects due to following reasons:

- (i) Its size is very small
 (ii) It has very high electronegativity
 (iii) Its dissociation energy in the molecular form (X_2) is the least.

31. Which has the maximum molar enthalpy of vaporisation?

- (a) HF (b) HCl (c) HBr (d) HI

32. Which halogen does not form any oxyacid?

- (a) Iodine (b) Bromine
 (c) Chlorine (d) Fluorine

Paragraph for Questions 33 and 34

The work done during adiabatic reversible process is

given by $W = \frac{nR[T_i - T_f]}{\gamma - 1}$. Thus, if $T_f > T_i$, then since

$1 - \gamma = -ve$ ($\because \gamma > 1$), the work is done on gas. Also if $T_f < T_i$, $W = -ve$, thus work is done by the gas. The

adiabatic process are more steeper than isothermal process and slope of adiabatic process = $\gamma \times$ slope of isothermal process *i.e.*, slope of adiabatic process $>$ slope of isothermal process (since $\gamma > 1$). Also the adiabatic process obey $PV^\gamma = \text{constant}$, whereas in isothermal process $PV = \text{constant}$.

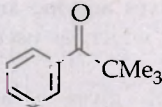
33. In an adiabatic expansion of air (assume it a mixture of N_2 and O_2), the volume increases by 5%. The percentage change in pressure is
 (a) 7% (b) 6%
 (c) 4% (d) 3%
34. In a thermodynamic process helium gas Obey's the law $\frac{T}{P^{2/5}} = \text{constant}$. The heat given to a gas when temperature of m moles of He is raised from T to $2T$ is
 (a) $8RT$ (b) $4RT$
 (c) $16RT$ (d) zero

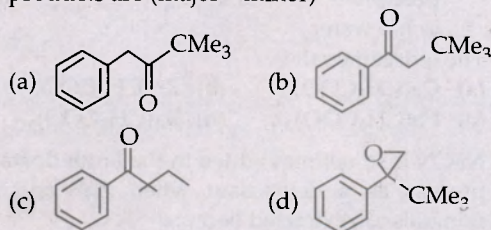
SECTION - III

Multiple Correct Answer Type

This section contains 6 multiple choice questions. Each question has four choices (a), (b), (c) and (d) out of which ONE or MORE are correct.

35. Which of the following methods give rise to 1-bromo-2-phenyl ethane?
 (a) Benzene + oxirane + H^+ followed by reaction with HBr
 (b) Benzene + oxirane + H^+ followed by reaction with P/Br_2
 (c) Propane + HBr followed by reaction with benzene in the presence of $AlCl_3$
 (d) Styrene + H_3O^+ + followed by reaction with P/Br_2 .
36. Given that $Ni^{2+}/Ni = -0.25$ V,
 $Cu^{2+}/Cu = 0.34$ V
 $Ag^+/Ag = 0.80$ V
 and $Zn^{2+}/Zn = -0.76$ V
 Which of the following reactions under standard conditions will not take place in the specified direction?
 (a) $Ni^{2+}_{(aq)} + Cu_{(s)} \rightarrow Ni_{(s)} + Cu^{2+}_{(aq)}$
 (b) $Cu_{(s)} + 2Ag^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$
 (c) $Cu_{(s)} + 2H^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + H_{2(g)}$
 (d) $Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)}$.
37. Ferroelectricity is exhibited by
 (a) barium titanate ($BaTiO_3$)
 (b) sodium potassium tartarate (Rochelle's salt)
 (c) potassium dihydrogen phosphate (KH_2PO_4)
 (d) lead zirconate ($PbZrO_3$).

38.  $\xrightarrow{CH_2N_2, \Delta}$ Products. The possible products are (major + minor)



39. Which of the following statement(s) is/are correct?
 (a) SO_3 is a stronger oxidising agent and more acidic than SO_2 .
 (b) Selenium forms only two oxo acids *i.e.*, selenous acid (H_2SeO_3) and selenic acid (H_2SeO_4).
 (c) The acidic strength and oxidising power of oxo acids is greater in + 6 oxidation state than in + 4 oxidation state.
 (d) The thermal stability of oxides of group 16 elements decreases in the order.
 $SO_2 > SeO_2 > TeO_2 > PoO_2$
40. Which of the following statement/s is/are not correct?
 (a) Physical adsorption is directly related to the critical temperature of the gas (adsorbate)
 (b) One gram of charcoal at $25^\circ C$ will always adsorb the same amount of a particular gas at a particular pressure.
 (c) At particular temperature, absorption always increases with increase of pressure.
 (d) In adsorption, the concentration of adsorbate is always greater at the surface of the adsorbent.

SOLUTIONS

PAPER-I

1. (a): At the top of the blast furnace (lowest temperature $\sim 500^\circ C$) the reaction is
 $3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$
2. (c): Ineffective shielding causes decrease in size.
3. (a): $CO_{2(g)} + C_{(s)} \rightleftharpoons 2CO_{(g)}$
 Initial pressure 0.5 atm
 At. eqm. $(0.5 - x)$ $2x$
 $\therefore (0.5 - x) + 2x = 0.8$ or $x = 0.3$ atm
 $\therefore p_{CO_2} = 0.5 - 0.3 = 0.2$,
 $p_{CO} = 2x = 2 \times 0.3 = 0.6$ atm
 $K = p_{CO} / p_{CO_2} = (0.6)^2 / 0.2 = 1.8$ atm

4. (c) : Enzymes being proteins contain the group $-\text{NH}-\text{CO}-$.

5. (b) : Y will be definitely ψ' because value of ψ cannot be negative, thus X will be ψ^2 and Z will be $4\pi r^2 \psi$. Z represent radial probability function; its value will be zero at origin.

6. (c) : ${}_c^a\text{X} \rightarrow {}_d^b\text{Y} + x {}_2^4\text{He} + y {}_0^1e_{-1}$

Here, $x = \alpha$ -particles emitted and $y = \beta$ -particles emitted.

$$a = b + 4x$$

$$x = \frac{a-b}{4}$$

$$c = d + 2x - y$$

$$y = d - c + 2x$$

$$y = d - c + \frac{a-b}{2}$$

$$y = d + \left[\frac{a-b}{2} \right] - c$$

7. (c) : BF_3 , AlCl_3 are electron deficient molecules while in PCl_5 and SF_6 molecules P and S possess more than 8 electrons in their valence shells.

8. (b) : Since B gives yellow ppt. with $\text{AgNO}_3/\text{HNO}_3$, B must be $\text{C}_6\text{H}_5\text{CH}_2\text{I}$ and hence A is $\text{C}_6\text{H}_5\text{I}$.

9. (d) : $-\text{OCH}_3$ is a better electron donating group than $-\text{CH}_3$ and NO_2 is better electron withdrawing group than $-\text{Cl}$.

10. (a) : Weight of $\text{CdCl}_2 = 1.5276 \text{ g}$
Weight of Cd in $\text{CdCl}_2 = 0.9367 \text{ g}$
Weight of Cl in $\text{CdCl}_2 = 0.5909 \text{ g}$

$$n(\text{Cl}) = \frac{0.5909}{35.453 \text{ g/mol}} = 0.016667 \text{ mol}$$

From the formula CdCl_2 we see that the number of moles of Cd is exactly half the number of moles of Cl.

$$n(\text{Cd}) = \frac{1}{2} n(\text{Cl}) = \frac{1}{2} (0.016667) = 0.008333 \text{ mol}$$

The atomic weight of Cd

$$= \frac{0.9367 \text{ g}}{0.008333} = 112.41 \text{ g/mol}$$

11. (d) : $w > z > y > x$

$-\text{CN}$ is more electron-withdrawing than $-\text{Cl}$.

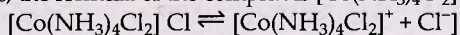
12. (c) : $\Delta T_f = i \times K_f \times m = i \times 1.86 \times 0.1$

$$\text{or } 0.372 = 0.186 \times i$$

$$\text{or } i = 2$$

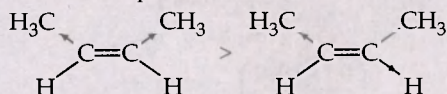
This shows that the complex gives two ions in solution.

Thus, the formula of the complex is $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$.



13. (a,b,c)

14. (a,b,c,d) : As magnitude of dipole moment increases, b.p. increases i.e.,

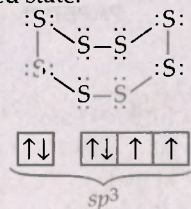


15. (a,c) : (b) is wrong because lyophilic sols have higher viscosity than that of the dispersion medium.

(d) is wrong because gold sol is irreversible as gold obtained back cannot be converted into sol by directly shaking with the dispersion medium.

16. (8) : The difference between number of lone pairs and number of S—S bonds in S_8 molecule is 8.

S_8 molecule is shown here. Every sulphur atom is in sp^3 hybridized state.



Thus, there are 8 S—S bonds and 16 lone pairs.
Difference = $16 - 8 = 8$.

17. (2) : Let the initial rate be :

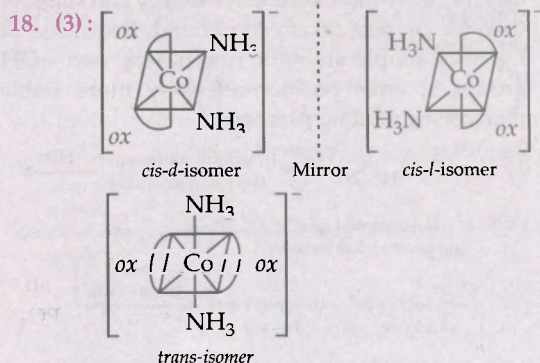
$$r_0 = k[A_0]^a$$

$$\frac{(r_0)_1}{(r_0)_2} = \frac{[A_0]_1^a}{[A_0]_2^a}$$

or

$$a = \frac{\log\{(r_0)_1 / (r_0)_2\}}{\log\{[A_0]_1 / [A_0]_2\}} = \frac{\log(2.40 \times 10^{-4} / 0.60 \times 10^{-4})}{\log(2 \times 10^{-3} / 1 \times 10^{-3})} = \frac{\log 4}{\log 2} = 2$$

\therefore The order of reaction = 2.



$$19. (2): \frac{(\Delta T)_P}{(\Delta T)_Q} = \frac{K_b \times \left(\frac{w_B \times 1000}{m_B \times w_A} \right)_P}{K_b \times \left(\frac{w_B \times 1000}{m_B \times w_A} \right)_Q}$$

$$\frac{0.2}{0.4} = \frac{\left(\frac{0.1 \times 1000}{100 \times 100} \right)_P}{\left(\frac{0.1 \times 1000}{100 \times m_B} \right)_Q}$$

$$\frac{1}{2} = \frac{(m_B)_Q}{100}$$

$$m_B = 50$$

$$\therefore (m_B)_P : (m_B)_Q = 100 : 50$$

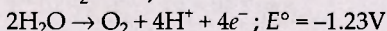
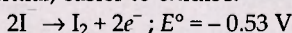
$$= 2 : 1$$

20. (3)

PAPER-II

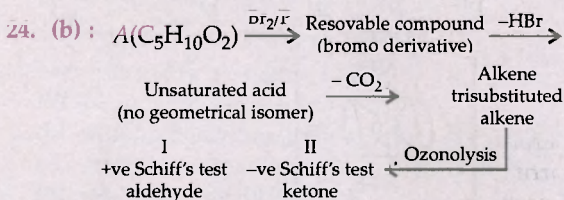
21. (c) : IE_3 of $Li(g)$
 Enthalpy of Li^{2+}
 $= 2.18 \times 10^{-18} \times 9 \text{ J atom}^{-1}$
 $= 2.18 \times 10^{-18} \times 9 \times 10^{-3} \times 6.023 \times 10^{23} \text{ kJ mol}^{-1}$
 $= 11817 \text{ kJ mol}^{-1}$
 And also $I_1 + I_2 + I_3$
 In all write $IE_1 + IE_2 + IE = 19600 \text{ kJ mol}^{-1}$
 and $IE_1 = 520 \text{ kJ mol}^{-1}$
 $\therefore IE_1 = 19600 - (11817 + 520)$
 $= 7263 \text{ kJ mol}^{-1}$

22. (a) : Either Mn^{2+} or H_2O will get reduced. Higher the reduction potential, easier to reduce. Thus H_2O will be reduced to give H_2 at cathode. Either I^- or H_2O will get oxidised. Higher the oxidation potential, easier to oxidise.



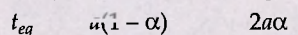
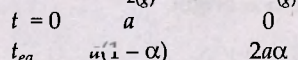
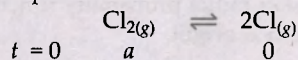
Thus, I^- will be oxidised to give I_2 at anode.

23. (d) : Higher the E° value, higher the reduction potential and greater the tendency to be reduced. II on reduction gives two aromatic rings which together have more resonance energy and stability than the present diketo compound. Reduction of I gives a simple aromatic ring having two -OH groups at *ortho* position-relatively more stable than corresponding *para* form.



Hence, A is $(CH_3)_2CH-CH_2-\overset{\overset{O}{\parallel}}{C}-OH$

25. (b) : Equilibrium of dissociation of Cl_2 may be represented as :



$$\text{Total moles} = a(1-\alpha) + 2a\alpha = a(1+\alpha)$$

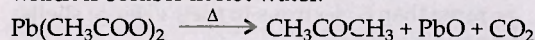
$$M_{mix} = \frac{aM_{Cl_2}}{a(1+\alpha)} = \frac{M_{Cl_2}}{(1+\alpha)}$$

$$\frac{R_{mix}}{R_{Kr}} = \sqrt{\frac{M_{Kr}}{M_{mix}}}$$

$$1.16 = \frac{84(1+\alpha)}{M_{Cl_2}}$$

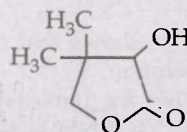
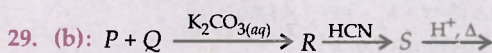
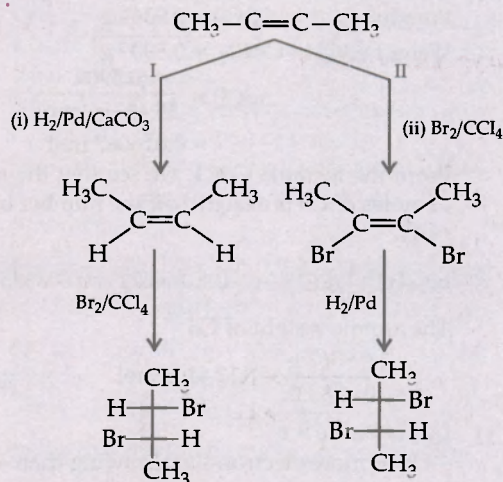
$$\frac{(1.16)^2 \times 71}{84} - 1 = \alpha, \alpha = 0.1374$$

26. (c) : The solution of lead acetate is sweet in taste, when HCl is added to its solution, it forms $PbCl_2$ which is soluble in hot water.

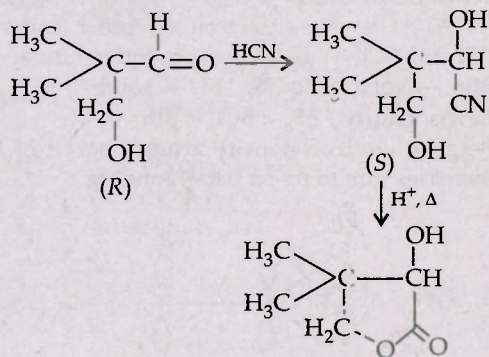
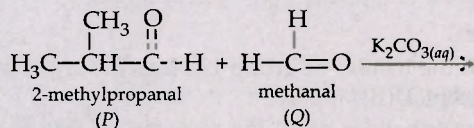


27. (d) : $NaCN$ is added as a depressant for zinc sulphide (ZnS). $NaCN$ forms a layer of zinc complex, $Na_2[Zn(CN)_4]$ on the surface of ZnS and thereby prevents it from forming the froth while PbS forms froth.

28. (a) :



R reacts with HCN so, it must contain $>C=O$ group. Since the compound S gives the given product formed on treatment with H^+ followed by heating thus S must have a $-CN$ group which on acidification gives $-COOH$ group with one carbon more than that in R. Therefore, P and Q are $(CH_3)_2CHCHO$ and $HCHO$ respectively.



30. (d)

31. (a)

32. (d)

33. (a): $PV^\gamma = \text{constant}$

$$p_1 \times \left[\frac{105V}{100} \right]^\gamma = \text{constant}$$

$$\therefore \frac{p_1}{p} \times \left[\frac{105}{100} \right]^\gamma = 1$$

$$\text{or } \frac{p_1}{p} = \left[\frac{105}{100} \right]^\gamma$$

$$\text{or } \frac{p_1}{p} = \left[\frac{105}{100} \right]^{7/5}$$

$$\therefore p_1 = 0.93p$$

$$\therefore 7\% \text{ decrease in } p$$

34. (b): $\frac{T}{p^{2/5}} = \text{constant}$

$$\text{or } T = \text{constant} \times p^{2/5}$$

$$\therefore PV = RT$$

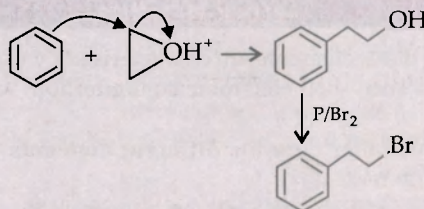
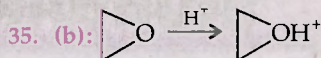
$$\therefore PV = R \times \text{constant } p^{2/5}$$

$$\therefore \frac{p}{p^{2/5}} \times V = \text{constant}$$

$$\text{or } PV^{5/3} = \text{constant} \quad \left(\because \gamma = \frac{5}{3} \text{ for He} \right)$$

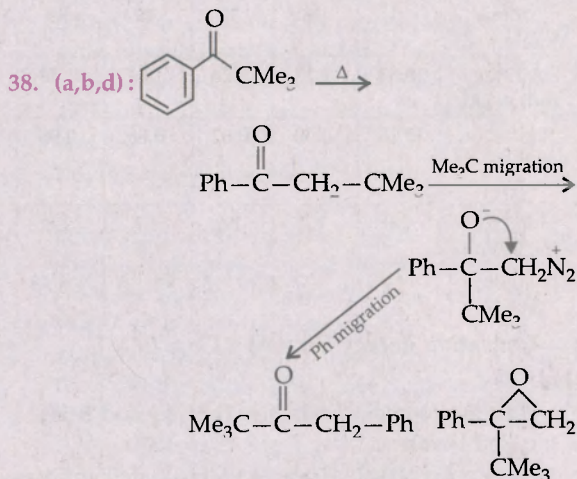
$$\text{or } PV^\gamma = \text{constant}$$

Thus, process is adiabatic $\therefore Q = 0$.



36. (a, c): These reactions (a) and (c) will have -ve emf and hence cannot take place in the specified direction.

37. (a,b,c)



39. (a,b,c): Thermal stability of the oxides of group 16 elements decreases in the order $\text{SO}_2 > \text{TeO}_2 > \text{SeO}_2 > \text{PoO}_2$ and not in the order as mentioned. TeO_2 decomposes at $> 733^\circ\text{C}$ while SeO_2 has $\sim 600^\circ\text{C}$ as the decomposition temperature. PoO_2 decomposes at 500°C .

40. (b,c,d): (b) is wrong because adsorption depends upon the surface area.

(c) is wrong because at about 0°C , adsorption remains constant after a particular pressure.

(d) is wrong because there can be negative adsorption also.

QUICK REVISION OF INORGANIC CHEMISTRY

PART-II

p-BLOCK ELEMENTS

- p-Block elements are characterised by the $ns^2 np^x$ valence shell electronic configuration, where
 $x = 1 - 6, n = 2 - 6$

But inner core for different elements may be different.

Group 13 : The Boron Family

- This group is the most metallic in nature of the p-block elements and only boron is non-metallic.

Property	B	Al	Ga	In	Tl
Atomic number (Z)	5	13	31	49	81
Atomic radius (Å)	0.82	1.18	1.26	1.44	1.48
Radius of trivalent ion (Å)	0.20	0.50	0.62	0.80	0.95
Electro-negativity	2.0	1.5	1.6	1.7	1.8
Oxidation states	+3	+3	+1, +3	+1, +3	+1, +3

- Ionisation energy** : $B > Al < Ga > In > Tl$

Hydrides

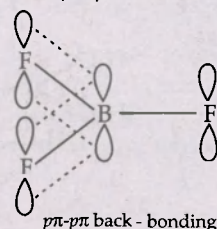
- B forms covalent hydrides, B_nH_{n+4} and B_nH_{n+6} called boranes.
- Al \rightarrow polymeric hydride $\rightarrow (AlH_3)_n$ - decomposes on heating.
- InH_3 and $TlH_3 \rightarrow$ extremely unstable.
- B, Al and Ga have the tendency to form complex anionic hydrides like $Li[AlH_4]$, $Li[BH_4]$, $Li[GaH_4]$ etc. due to the presence of a nascent p-orbital in their outermost shells due to which these readily accepts electron pair from the hydride ion (H^-) as
 $AlH_3 + H^- \longrightarrow [AlH_4]^-$ [Here, A = Al, Ga and B]

Oxides and hydroxides

- Oxides** (M_2O_3 type):
 $B_2O_3 \rightarrow$ acidic
 Al_2O_3 and $Ga_2O_3 \rightarrow$ amphoteric
 In_2O_3 and $Tl_2O_3 \rightarrow$ strong basic
- Hydroxides** ($M(OH)_3$ type):
 $Tl \rightarrow Tl(OH)_3$ and $TlOH$

Halides

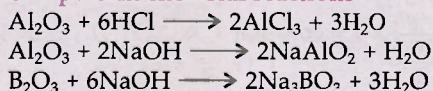
- All the halides of group 13 elements are known except $Tl(III)$ iodide.
- The trihalides of all the elements of this group act as Lewis acids.
 $B > Al > Ga > In \rightarrow$ electron accepting tendency
 BF_3 and $BCl_3 \rightarrow$ gases at room temperature.
 $BBr_3 \rightarrow$ volatile liquid; $BI_3 \rightarrow$ solid
- Lewis acidity** : $BF_3 < BCl_3 < BBr_3 < BI_3$
 Because electron-density around boron in BF_3 increases due to $p\pi-p\pi$ back-bonding.

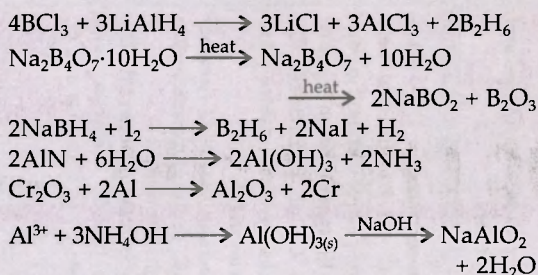


The tendency of back-donation decreases to BCl_3 and BBr_3 because the energy difference between fully-filled orbital of halogen ($Cl-3p$, $Br-4p$) and vacant orbital of $B-2p$ increases.

- Trihalides of Al exist in dimeric form both in vapour state and in non-polar solvent.
- $[AlF_6]^{3-}$, $[GaCl_6]^{3-}$ and $[InCl_6]^{3-}$ are formed by Al, Ga and In due to the availability of vacant d-orbital in central atoms.
- Due to the small size and inability to accommodate energy, BCl_3 does not change from covalent compound to ion formation in aqueous solution (as occurs in $AlCl_3$).
- Al, Ga, In and Tl ions exist as octahedral aqua ions i.e. $[M(OH_2)_6]^{3+}$ in aqueous solution and many salts like halides, sulphates, nitrates and perchlorates exist as hydrates.
- Aluminium sulphates form double salts called alum with salts of other metals.
- Alums $[M_2SO_4 \cdot M_2(SO_4)_3 \cdot 24H_2O] \rightarrow$ used for softening of hard water and as mordant in dyeing and printing of textiles.

Some important chemical reactions

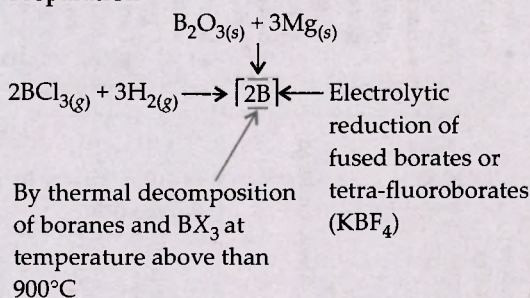




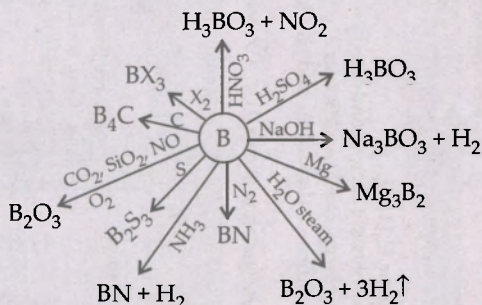
BORON

2 isotopic forms \rightarrow ^{10}B (19%) and ^{11}B (81%).

Preparation

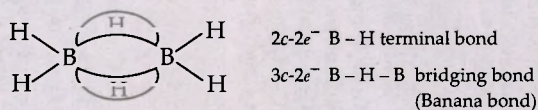


Properties

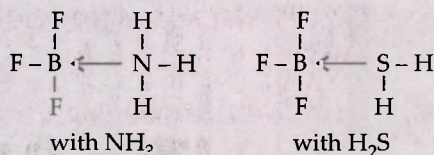


Boranes

- The compound $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$ is ionic and exist as $[\text{H}_3\text{N} \rightarrow \text{BH}_2 \leftarrow \text{NH}_3]^+ [\text{BH}_4]^-$ and forms borazine on heating.
 - Boron nitride (inorganic graphite) structure resembles graphite.
 - Borazine or borazole or inorganic benzene
- $$3\text{BCl}_3 + 4\text{NH}_4\text{Cl} \longrightarrow \boxed{\text{B}_3\text{N}_3\text{H}_6} \xleftarrow{3\text{NaBH}_4 + 4\text{NH}_4\text{Cl}}$$
- Boranes are electron deficient compounds.



BF_3 , being electron deficient compound, can accept a lone pair of electron, thus behaves as Lewis acid and also used as catalyst in organic reactions. It can form complexes like



- $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ (Borax)
Water softener and cleansing agent.
- Borax bead test**

$$\text{Na}_2\text{B}_4\text{O}_7 \xrightarrow[\text{Transparent bead}]{\text{Borax}, \Delta, 740^\circ\text{C}} 2\text{NaBO}_2 + \text{B}_2\text{O}_3$$

$$\text{B}_2\text{O}_3 + \text{CoO} \longrightarrow \text{Co(BO}_2)_2 : \text{blue bead}$$

$$\text{B}_2\text{O}_3 + \text{MnO} \longrightarrow \text{Mn(BO}_2)_2 : \text{pink bead}$$

Boric acid or orthoboric acid, H_3BO_3

- A weak monobasic acid. It does not donate protons like most acids but rather it accepts pair of electron from OH^- . It is therefore, a Lewis acid, and is better written as B(OH)_3 .

$$\text{B(OH)}_3 + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + [\text{B(OH)}_4]^-$$
, $\text{pK}_a = 9.25$
- The titration between B(OH)_3 and a strong alkali solution (e.g. NaOH) is not possible, because sodium metaborate $\text{Na}^+[\text{B(OH)}_4]^-$ or $[\text{NaBO}_2 \cdot 2\text{H}_2\text{O}]$ formed by reaction between B(OH)_3 and NaOH gets hydrolysed to regenerate B(OH)_3 and NaOH .

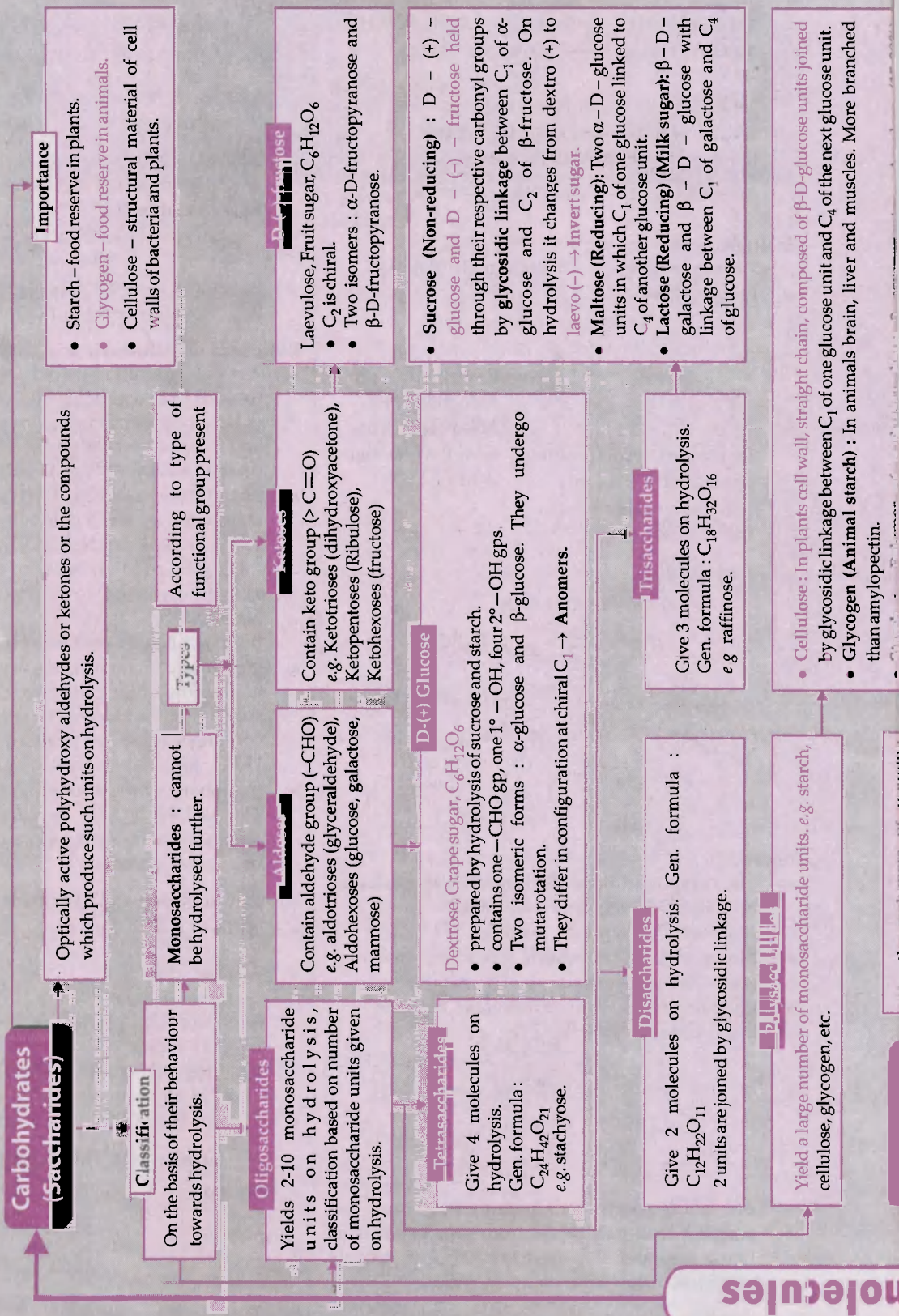
$$\text{B(OH)}_3 + \text{NaOH} \rightleftharpoons \text{Na}^+[\text{B(OH)}_4]^-$$
- However, if some quantity of polyhydroxy compound, like catechol, glycerol, mannitol, sugar etc, is added to the titration solution, the complex compound gives H^+ ions which makes H_3BO_3 to behave as a strong acid.
- Orthoboric acid contains triangular BO_3^{3-} units. In the solid the B(OH)_3 units are hydrogen bonded together into two dimensional sheets with almost hexagonal symmetry.

Aluminium oxide and hydroxide

- $$\text{Al(OH)}_3 \xrightarrow[\text{Corundum}]{450^\circ\text{C}, \Delta} \gamma - \text{Al}_2\text{O}_3 \xrightarrow[1000^\circ\text{C}, \Delta]{1000^\circ\text{C}} \alpha - \text{Al}_2\text{O}_3$$
- Alums**
General formula : $\text{M(I)} \text{M' (III)} (\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $[\text{M(H}_2\text{O)}_6]^+$, $[\text{M'(H}_2\text{O)}_6]^{3+}$ and SO_4^{2-} in 1 : 1 : 2 ratio.
e.g. $\text{M(I)} = \text{K}^+$ or NH_4^+ , $\text{M' (III)} = \text{Al}^{3+}$
Used as mordant in dyeing.
- Cement : $\text{Ca}_3\text{Al}_2\text{O}_6$ - Tricalcium aluminate

Group 14 : The Carbon Family

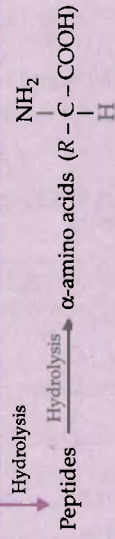
Property	C	Si	Ge	Sn	Pb
Atomic number (Z)	6	14	32	50	82
Atomic radius (Å)	0.77	1.17	1.22	1.41	1.44



acids connected to each other by peptide bond or peptide linkage.

Proteins

Hydrolysis



Types

- **Essential amino acids (10)** : Which cannot be synthesized in the body and must be obtained through diet.
- **Non-essential amino acids (10)** : (Dispensable) can be synthesized by body.

(water soluble) : unbranched chain polymer and amylopectin (80-85%)
(water insoluble) : branched chain polymer.

Classification

- Based on molecular structure.
- **Fibrous** : Thread like e.g. keratin, collagen, myosin, etc.
 - **Globular** : Spheroidal e.g. enzymes, hormones, Hb, antibodies, albumin, etc.

Structure

- **Primary** : Sequence of α -amino acids.
- **Secondary** : Shape due to H-bonding.
- **Tertiary** : Overall folding of the polypeptide chains (secondary structure).
- **Quaternary** : Spatial arrangement of subunits *w.r.t.* each other.

Denaturation

Due to coagulation, native shape of the protein is destroyed and biological activity is lost (2° and 3° structures destroyed, 1° remains intact).

Types

α -Helix

formed due to intramolecular H-bonds between the $\text{C}=\text{O}$ of one amino acid residue and the $\text{N}-\text{H}$ of the 4th amino acid residue in the chain. e.g., α -keratin in hair, myosin in muscles.

β -Pleated sheet

Formed due to intermolecular H-bonds between two neighbouring polypeptide chains in a zig-zag manner. e.g., silk protein fibroin.

DNA

- Sugar is β -D-2-deoxyribose.
- 4 bases are :
Purines : Adenine (A), Guanine (G),
Pyrimidines : Cytosine (C), Thymine (T).

RNA

- Sugar is β -D-ribose.
- 3 bases are same + fourth one is Uracil (U) instead of Thymine (T).

- **Chargaff Rule** : Total amount of purines = pyrimidines (A+G) (C+T)
- **Double helical structure** : By Watson, Crick and Wilkins. Pairing between C=G and A=T

Nucleic Acids/ Polynucleotides

(Pentose sugar + Base + Phosphoric acid)

Electro-negativity	2.5	1.8	1.8	1.8	1.8
Oxidation states	+4	+4	+2, +4	+2, +4	+2, +4

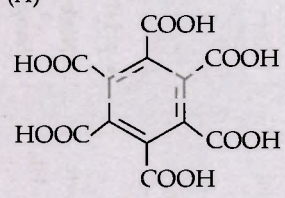
- The variable oxidation states are seen due to inert pair effect.
- C and Si → non-metals, Ge → semi-metal, Sn and Pb → metals. Metallic character increases down the group.
- The covalent nature in the compounds of Sn^{4+} and Pb^{4+} ions is due to high polarisation produced by them.
- As we move down the group stability of lower oxidation state increases due to inert pair effect.
- Catenation** : $\text{C} \gg \text{Si} > \text{Ge} \approx \text{Sn} \gg \text{Pb}$
- Except C, all other elements form complexes due to presence of vacant d -orbitals in them *i.e.*, these behaves as Lewis acids.
e.g. $\text{SiF}_4 \xrightarrow{\text{forms}} [\text{SiF}_6]^{2-}$, octahedral structure sp^3d^2 hybridisation
- Allotropic forms**
C → crystalline and microcrystalline
Si → crystalline and amorphous
Ge → 2 crystalline forms
Sn → 3 solid forms → grey tin, white tin and rhombic tin
- Artificial diamonds prepared by Moissan's method.
Artificial graphite → Acheson process
- Semiconductor grade Si is prepared by the reduction of highly pure $\text{SiCl}_4/\text{SiHCl}_3$ with H_2 or by the pyrolysis of SiH_4 mainly.

Multiple bonding

- C has strong tendency to show $p\pi-p\pi$ multiple bond either with itself ($\text{C}=\text{C}$, $\text{C}\equiv\text{C}$) or with atoms like N, O ($\text{C}\equiv\text{N}$, $\text{C}=\text{O}$ etc.) Carbon does not have d -orbitals and never forms $d\pi-p\pi$ or $d\pi-d\pi$ bonds. Silicon on the other hand forms $d\pi-d\pi$ bonds.
- In case of $\text{N}(\text{CH}_3)_3$, geometry is pyramidal but in case of $\text{N}(\text{SiH}_3)_3$ it is planar because the lone pair of N-atom is transferred to the empty d -orbitals of silicon. ($p\pi-d\pi$ overlapping).

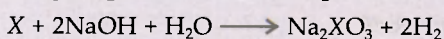
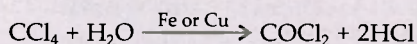
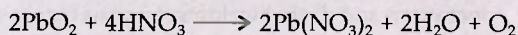
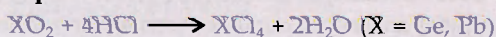
Oxides	Nature
CO , CO_2 , SiO_2	acidic
GeO , GeO_2 , SnO , SnO_2 , Pb_3O_4	amphoteric
PbO , PbO_2	basic

- Stability of tetrahalides
 $\text{CX}_4 > \text{SiX}_4 > \text{GeX}_4 > \text{SnX}_4 > \text{PbX}_4$
- Elements in this group are relatively unreacted but reactivity increases down the group. Pb often appears more noble than expected due to a surface coating of oxide and partly due to high over potential for the reduction of H^+ to H_2 at a lead surface.
- Reactivity of the elements of group 14 (IVA)

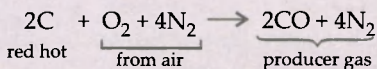
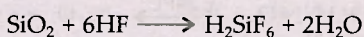
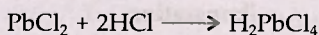
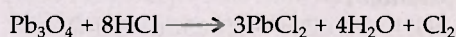
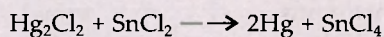
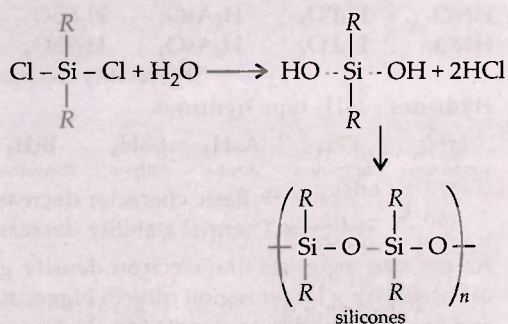
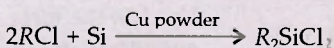
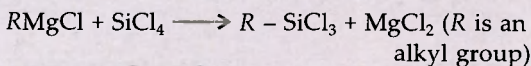
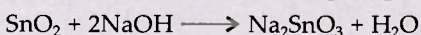
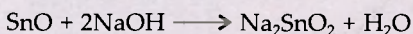
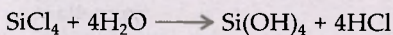
Reagent	Reactivity
H_2O	C, S, Ge, Pb unaffected by H_2O .
	$\text{Sn} + 2\text{H}_2\text{O} \xrightarrow{\text{(steam)}} \text{SnO}_2 + 2\text{H}_2$
Dilute acids	C, Si, Ge unaffected by dilute acids.
	Pb does not dissolve in dilute H_2SO_4 due to formation of PbSO_4 coating.
Concentrated acids	Diamond is unaffected by concentrated acids, but graphite changes to mellitic acid ($\text{C}_{12}\text{H}_6\text{O}_{12}$) also called benzene hexa-carboxylic acid (A)
	 <p>(A)</p>
	with hot concentrated HNO_3 and to graphite oxide with hot concentrated HF/HNO_3 .
	Si is oxidised and changes to SiF_4 by hot concentrated HNO_3/HF .
Alkalies	Pb does not dissolve in concentrated HCl due to formation of PbCl_2 coating.
	Carbon is unaffected by alkalies.
Complex formation	Sn and Pb are slowly attacked by cold alkali, and rapidly by hot alkali, giving stannates $\text{Na}_2[\text{Sn}(\text{OH})_6]$ and plumbates $\text{Na}_2[\text{Pb}(\text{OH})_6]$.
	Si, Ge, Sn and Pb can show coordination number more than 4. Example : Si - Ge (6), Sn - Pb (8)

Halogens	Diamond is unreactive, but graphite reacts forming $(CF)_n$.
	Si and Ge form volatile SiX_4 and GeX_4 .
	Sn and Pb are less reactive. Sn reacts with Cl_2 and Br_2 in cold, and with F_2 and I_2 on warming. Lead reacts with F_2 in cold and with Cl_2 on heating forming PbX_2 .

Important chemical reactions



(X = Si, Sn)



- Hydrides of Ge are called germanes, $[Ge_nH_{2n+2}]$ $n = \text{upto } 5$ are known.

Group 15 : The Nitrogen Family

- They are called **pnictogens**.

Electronic configuration of elements of group 15

Element	Atomic number	Electronic configuration	Oxidation No.
Nitrogen (N)	7	$[He] 2s^2 2p^3$	+1, +2, +3, -3, +4, +5
Phosphorus (P)	15	$[Ne] 3s^2 3p^3$	+3, -3, +4, +5
Arsenic (As)	33	$[Ar] 3d^{10} 4s^2 4p^3$	+3, -3, +5
Antimony (Sb)	51	$[Kr] 4d^{10} 5s^2 5p^3$	+3, -3, +5
Bismuth (Bi)	83	$[Xe] 4f^{14} 5d^{10} 6s^2 6p^3$	+3, +5

General characteristics of group 15 elements

- The elements of group 15 are less metallic than the corresponding elements of group 14. On moving down the group, the metallic character increases.

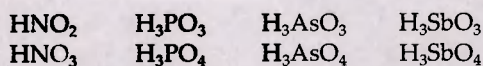
N	P	As	Sb	Bi
Non-metals		Metalloids		Metal

- Allotropy** : Except nitrogen and bismuth, all elements of this group show allotropy. Phosphorus exists in three allotropic forms, *i.e.*, white, red and black phosphorus. Arsenic and antimony exist in two allotropic forms, *i.e.*, yellow and grey.
- Oxides** : All these elements form oxides of the type X_2O_3 , X_2O_4 and X_2O_5 .

N_2O_3	P_2O_3	As_2O_3	Sb_2O_3	Bi_2O_3	Acidic nature increases ↓
N_2O_4	P_2O_4	As_2O_4	Sb_2O_4	Bi_2O_4	
N_2O_5	P_2O_5	As_2O_5	Sb_2O_5	Bi_2O_5	
Acidic nature decreases →					

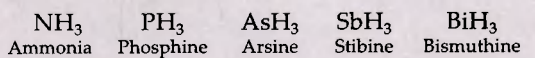
As electronegativity increases, acidic character of the oxide increases. Among the oxides of same element, higher the oxidation state, greater the acidic character.

- Oxoacids** : The strength and stability of oxoacids having the elements in the same oxidation states decreases gradually with decrease in electronegativity of the central atom.



—————→ Stability decreases

● **Hydrides** : MH_3 type hydrides



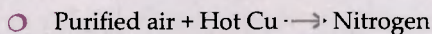
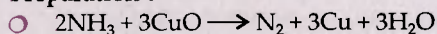
—————→ Basic character decreases.

—————→ Thermal stability decreases.

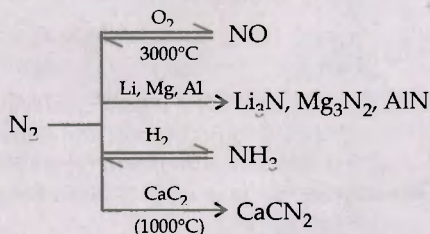
As the size increases, the electron density gets diffused over a larger region (due to bigger size) and hence the ability to donate the electron pair (basic nature) decreases.

Nitrogen (N_2)

● **Preparation** :



● **Properties** :



- **Uses** : Because of unreactive nature, it is used to provide an inert atmosphere in certain metallurgical operations and during welding. Used as blanketing gas.

Some important compounds of group 15 elements

Compound	Preparation	Properties	Uses
N_2O (Laughing gas)	$\text{NH}_4\text{NO}_3 \xrightarrow{\Delta, 250^\circ\text{C}} \text{N}_2\text{O} + 2\text{H}_2\text{O}$	$\text{NaN}_3 \xrightarrow{\text{H}^+} \text{N}_3\text{H}$ $\text{N}_2\text{O} \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{N}_2\text{O}_2$ $\text{N}_2\text{O} \xrightarrow{\Delta} \text{N}_2 + \text{O}_2$	Used as anaesthetic, propellant
N_2O_5	$2\text{HNO}_3 \xrightarrow[\text{low temp.}]{\text{P}_2\text{O}_5} \text{N}_2\text{O}_5 + \text{HPO}_3$	$\text{NaNO}_3 + \text{NO}_2\text{Cl}$ $\text{N}_2\text{O}_5 \xrightarrow{\text{O}_3} \text{NO}_3 + \text{O}_2$ (radical) $\text{N}_2\text{O}_5 \xrightarrow{\Delta} \text{NO}_2 + \text{O}_2 + \text{NO}$ $\text{N}_2\text{O}_5 \xrightarrow{\text{H}_2\text{O}} \text{HNO}_3$	Used in the form of anhydride of HNO_3
NH_3	$\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \longrightarrow 2\text{NH}_3$ $\Delta H_f^\circ = -46.1 \text{ kJ/mol}$ (Haber's process)	$[\text{Ag}(\text{NH}_3)_2]^+ \xrightarrow{\text{AgCl}} \text{NH}_3$ $\text{NH}_3 \xrightarrow{\text{O}_2} \text{N}_2$ $\text{NH}_3 \xrightarrow{\text{H}_2\text{O}_2} \text{HNO}_2$ $\text{NH}_3 \xrightarrow{\text{H}_2\text{O}} \text{HNO}_3$ $\text{NH}_3 \xrightarrow{\text{O}_2, \text{Pt}} \text{NO}$ $\text{NH}_3 \xrightarrow{\text{O}_2} \text{NH}_4\text{Cl} + \text{N}_2$ (if NH_3 in excess) $\text{NH}_3 \xrightarrow{\text{K}_2\text{HgI}_4} \text{brown ppt.}$ $\text{NH}_3 \xrightarrow{\text{KOH}} \text{K}_2\text{HgI}_4$	Used in refrigerators, manufacturing of rayon, HNO_3 , NaHCO_3 , nitrogenous fertilizers
PH_3	$\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O} \longrightarrow 3\text{Ca}(\text{OH})_2 + 2\text{PH}_3$	$\text{NH}_4\text{PH}_2 \xrightarrow{\text{NH}_3} \text{PH}_3$ $\text{PH}_3 \xrightarrow{\Delta} \text{P}_4 + \text{H}_2$ $\text{PH}_3 \xrightarrow{\text{HCl}} \text{PH}_4^+\text{Cl}^-$ $\text{PH}_3 \xrightarrow{\text{H}_2\text{O}} \text{H}_3\text{PO}_4$ $\text{PH}_3 \xrightarrow{\text{Ag}^+} \text{Ag} + \text{H}_3\text{PO}_3$ $\text{PH}_3 \xrightarrow{\text{Cu}^{2+}} \text{Cu} + \text{H}_3\text{PO}_4$	Used as dehydrating agent
PCl_5	$\text{P}_4 + 10\text{Cl}_2 \longrightarrow 4\text{PCl}_5$ (white or red)	$\text{PCl}_5 \xrightarrow{\text{H}_2\text{O}} \text{H}_3\text{PO}_4 + \text{HCl}$ $\text{PCl}_5 \xrightarrow{\text{P}_2\text{S}_5} \text{PSCl}_3$ $\text{PCl}_5 \xrightarrow{\text{SO}_2} \text{SOCl}_2 + \text{POCl}_3$ $\text{PCl}_5 \xrightarrow{\text{P}_4\text{O}_{10}} \text{POCl}_3$	Used as chlorinating and dehydrating agent

Group 16 : The Oxygen Family

- The first four elements of this group are non-metallic in character (O, S, Se, Te) and are collectively called as **chalcogens**, i.e. ore forming elements.

Element	Atomic number	Electronic configuration	Oxidation states
Oxygen (O)	8	[He] $2s^2 2p^4$	-2
Sulphur (S)	16	[Ne] $3s^2 3p^4$	-2, +2, +4, +6
Selenium (Se)	34	[Ar] $3d^{10} 4s^2 4p^4$	-2, +2, +4, +6
Tellurium (Te)	52	[Kr] $4d^{10} 5s^2 5p^4$	-2, +3, +4, +6
Polonium (Po)	84	[Xe] $4f^{14} 5d^{10} 6s^2 6p^4$	+2, +4

General characteristics of group 16 elements

- Oxygen has a great tendency to form $p\pi-p\pi$ double bond but other elements do not, due to their larger size. However S and other elements have vacant d -orbitals and form $p\pi-d\pi$ multiple bonds. But their tendency to form $p\pi-d\pi$ multiple bonds decreases from S to Te.
- Allotropy** : All the elements of the group 16 exhibit allotropy.
 - Oxygen exists as O_2 and O_3 .
 - Sulphur exists in a number of allotropic forms, such as rhombic, monoclinic, plastic sulphur.
 - Selenium : Red and grey (both non-metallic).

- Tellurium : Crystalline and amorphous.
- Polonium : α and β (both metals).

- Hydrides** : Elements of group 16 form hydrides of general formula H_2M such as H_2O , H_2S , H_2Se , H_2Te and H_2Po . Water is colourless, odourless liquid while hydrides of the other elements of this group are colourless, bad smelling, poisonous gases. Acidic nature of hydrides increases while thermal stability decreases down the group. All hydrides except H_2O act as reducing agent and reducing character increases down the group.
- Halides** : The elements of group 16 form a variety of halides. Formulae of known halides of this group are given in the table.

Element	Fluorine	Chlorine	Bromine	Iodine
Oxygen	F_2O	Cl_2O , ClO_2 , Cl_2O_7	Br_2O	I_2O_5
Sulphur	SF_6 , S_2F_{10} , SF_4 , S_2F_2	SCl_4 , SCl_2 , S_2Cl_2	S_2Br_2	—
Selenium	SeF_6 , SeF_4 , Se_2Fe_2	$SeCl_4$, $SeCl_2$, Se_2Cl_2	$SeBr_4$, $SeBr_2^*$, Se_2Br_2	—
Tellurium	TeF_6 , Te_2F_{10} , TeF_4	$TeCl_2^*$, $TeCl_4$	$TeBr_4$, $TeBr_2$	TeI_4
Polonium	PoF_6	$PoCl_4$, $PoCl_2$	$PoBr_4$, $PoBr_2$	PoI_4
* Unstable				

Dioxygen/Oxygen (O_2)

- Oxygen is the first element of group 16. Joseph Priestly prepared it by heating mercury oxide with the help of the sun rays and gave it the name oxygen.
 - Preparation** :
 - $2HgO \xrightarrow{725\text{ K}} 2Hg + O_2$
 - $2KClO_{3(s)} \xrightarrow[420\text{ K}]{\text{MnO}_2} 2KCl_{(s)} + 3O_{2(g)}$
 - $2H_2O \xrightarrow{\text{electrolysis}} 2H_{2(g)} + O_{2(g)}$
- O_2 — $\xrightarrow{Na} Na_2O$
 $\xrightarrow{Fe} Fe_2O_3$
 $\xrightarrow{\text{strong heating}} H_2, 1073\text{ K} \rightarrow H_2O$
 $\xrightarrow{P_4 (\text{hot})} P_2O_5$
 $\xrightarrow{CS_2 (\text{hot})} CO_2 + SO_2$
 $\xrightarrow{CH_4} CO_2 + H_2O + 890\text{ kJ}$
- Uses** : It is used in steel making, as oxidiser in rocket propellants and in fuel cells. It is used

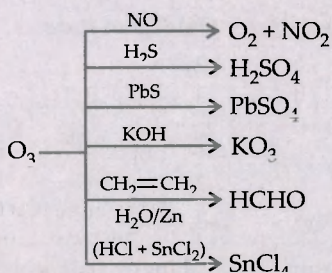
in oxy-hydrogen and oxy-acetylene welding torches.

Compounds	Oxidation state of O
In oxides	-2
In peroxides	-1
In superoxides	-1/2
In dioxygen	0
In oxygen difluoride	+2
In oxygen monofluoride	+1

Ozone (O_3)

- Oxygen is never completely converted into ozone and we always obtain a mixture of oxygen and ozone. This mixture is called ozonised oxygen.

$$3O_2 \xrightleftharpoons{\text{Electric discharge}} 2O_3, \Delta H = +284.5\text{ kJ}$$
- Properties** : Pure ozone is a blue gas, with a strong irritating smell. It is about 1.5 times heavier than air. It is more soluble than oxygen in water.



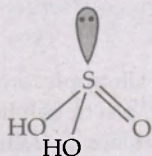
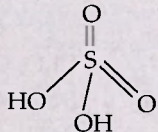
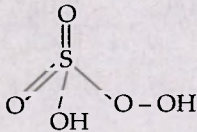
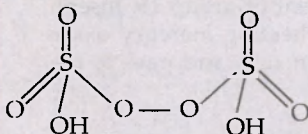
- **Uses :** It is used for sterilizing drinking water, for bleaching delicate fabrics, for purifying air

at the crowded places, for preservation of meat in cold storages.

Key Points

- Fluorides are the most stable, while iodides are the least stable among halides of group 16 elements.
- Sulphur exists as S_8 and has puckered ring structure.
- Volatility order is $\text{H}_2\text{O} < \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$.
- Se and Te are called photosensitive elements.

Oxoacids of sulphur

Oxoacid	Oxidation state, basicity and salt type	Structure	Properties
Sulphurous acid H_2SO_3	S = +4, dibasic, and forms two series of salts, sulphites (SO_3) and bisulphites (HSO_3)		<ul style="list-style-type: none"> – acts as reducing agent as well as oxidising agent – free acid does not exist
Sulphuric acid H_2SO_4 (oil of vitriol)	S = +6, dibasic and forms two series of salts, sulphates (SO_4) and bisulphates (HSO_4)		<ul style="list-style-type: none"> – stable, acts as oxidising agent and dehydrating agent
Peroxomonosulphuric acid H_2SO_5 or Caro's acid	S = +6, monobasic and forms single type of salt, peroxy disulphates		<ul style="list-style-type: none"> – stable crystalline and hygroscopic solid – powerful oxidizing agent
Peroxodisulphuric acid $\text{H}_2\text{S}_2\text{O}_8$ or Marshall's acid	S = +6 and forms single type of salt, peroxydisulphates ($\text{S}_2\text{O}_8^{2-}$)		<ul style="list-style-type: none"> – stable crystalline and hygroscopic solid – strong oxidizing agent

Group 17 : The Halogens Family

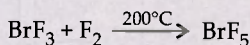
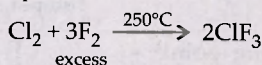
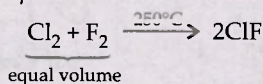
- The general valence shell electronic configuration of group 17 is $ns^2 np^5$ (where $n = 2$ to 6).

Element	Atomic number	Electronic configuration	Oxidation states
Fluorine (F)	9	[He] $2s^2 2p^5$	-1
Chlorine (Cl)	17	[Ne] $3s^2 3p^5$	-1, +1, +3, +5, +7
Bromine (Br)	35	[Ar] $3d^{10} 4s^2 4p^5$	-1, +1, +3, +5, +7
Iodine (I)	53	[Kr] $4d^{10} 5s^2 5p^5$	-1, +1, +3, +5, +7
Astatine (At)	85	[Xe] $4f^{14} 5d^{10} 6s^2 6p^5$	-

- **Interhalogen compounds :** The halogens, on account of difference in their electronegativities, combine with each other and form a binary covalent compounds of AB_n type which are called interhalogen compounds. A is always bigger atom and B is smaller atom and n may have values 1, 3, 5, 7 corresponding to oxidation states of halogens.

- All the interhalogen compounds except IF_7 can be prepared by direct combination of halogens under appropriate conditions.

Example :



Interhalogen compounds

Molecule	Total no. of electron pairs around X	Bond pairs	Lone pairs	Shape	Example
XY	4	1	3	Linear	ClF , BrF , BrCl , ICl , IBr
XY_3	5	3	2	T-shaped	ClF_3 , BrF_3 , ICl_3
XY_5	6	5	1	Square pyramidal	BrF_5 , IF_5
XY_7	7	7	0	Pentagonal	IF_7

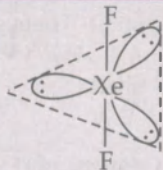
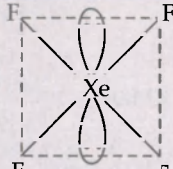
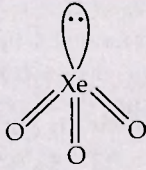
Key Points

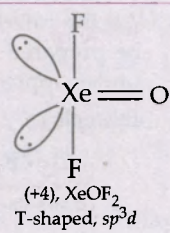
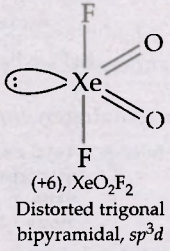
- Electron affinity : $\text{F} < \text{Cl} > \text{Br} > \text{I}$
- Oxidising power : $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
- Reducing power : $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$
- I_2 is soluble in KI solution due to formation of KI_3 (or I_3^-).
- Interhalogen compounds are more reactive than the constituent halogens because $\text{X}-\text{Y}$ bond is weaker than $\text{X}-\text{X}$ or $\text{Y}-\text{Y}$.

Group 18 : Inert Gases

Element	Atomic number	Electronic configuration
Helium (He)	2	$1s^2$
Neon (Ne)	10	$1s^2 2s^2 2p^6$
Argon (Ar)	18	$1s^2 2s^2 2p^6 3s^2 3p^6$
Krypton (Kr)	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$
Xenon (Xe)	54	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$
Radon (Rn)	86	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$

Compounds of xenon

Compound	Preparation	Properties	Structure
XeF_2 , Xenon difluoride	$\text{Xe} + \text{F}_2 \xrightarrow[400^\circ\text{C}]{\text{Ni tube}} \text{XeF}_2$ $\text{Xe} + \text{F}_2 \xrightarrow[\text{discharge}]{\text{Electric}} \text{XeF}_2$ $\text{Xe} + \text{F}_2 \xrightarrow[\text{(Hg vapour)}]{h\nu} \text{XeF}_2$	$\text{XeF}_2 \xrightarrow{\text{H}_2} \text{Xe} + 2\text{HF}$ $\text{XeF}_2 \xrightarrow{\text{H}_2\text{O}} \text{Xe} + 2\text{HF} + \frac{1}{2}\text{O}_2$ $\text{XeF}_2 \xrightarrow{\text{I}_2} 2\text{IF} + \text{Xe}$ $\text{XeF}_2 \xrightarrow{2\text{HCl}} \text{Xe} + 2\text{HF} + \text{Cl}_2$ <p>– Acts as fluorinating agent.</p>	 <p>(+2), XeF_2 Linear, sp^3d</p>
XeF_4 , Xenon tetrafluoride	$\text{Xe} + \text{F}_2 \xrightarrow[600^\circ\text{C}]{\text{Ni tube}} \text{XeF}_4$ $\text{Xe} + \text{F}_2 \xrightarrow[-78^\circ\text{C}]{\text{Electric discharge}} \text{XeF}_4$	<p>– Colourless, crystalline solid with melting point = 117.1°C</p> <p>– $\text{XeF}_4 + 2\text{H}_2 \rightarrow \text{Xe} + 4\text{HF}$</p> <p>– Undergoes disproportionation in water $2\text{XeF}_4 + 3\text{H}_2\text{O} \rightarrow \text{Xe} + \text{XeO}_3 + 6\text{HF} + \text{F}_2$</p> <p>– Gives adduct $\text{XeF}_4 + \text{SbF}_5 \rightarrow [\text{XeF}_3]^+ [\text{SbF}_6]^-$</p> <p>– Acts as oxidising and fluorinating agent</p> <p>– Dissolves in anhydrous HF</p>	 <p>(+4), XeF_4 Square planar, sp^3d^2</p>
XeO_3 , Xenon trioxide	<p>Complete hydrolysis of XeF_4 and XeF_6</p> $2\text{XeF}_4 + 3\text{H}_2\text{O} \rightarrow \text{XeO}_3 + \text{Xe} + \text{F}_2 + 6\text{HF}$ $\text{XeF}_6 + 3\text{H}_2\text{O} \rightarrow \text{XeO}_3 + 6\text{HF}$	<p>– Colourless, highly explosive and powerful oxidising agent</p> <p>– With water forms xenic acid $\text{XeO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{XeO}_4$</p> <p>– Undergoes disproportionation when dissolved in alkali $2\text{XeO}_3 + 4\text{OH}^- \rightarrow \text{Xe} + \text{O}_2 + \text{XeO}_6^{4-} + 2\text{H}_2\text{O}$</p>	 <p>(+6), XeO_3 Trigonal pyramidal, sp^3</p>

XeOF ₂ , xenon oxydifluoride	Partial hydrolysis of XeF ₄ $\text{XeF}_4 + \text{H}_2\text{O} \xrightarrow{-80^\circ\text{C}} \text{XeOF}_2 + 2\text{HF}$	- Unstable	 (+4), XeOF ₂ T-shaped, sp ³ d
XeO ₂ F ₂ xenon dioxy- difluoride	- Partial hydrolysis of XeOF ₄ or XeF ₆ $\text{XeOF}_4 + \text{H}_2\text{O} \longrightarrow \text{XeO}_2\text{F}_2 + 2\text{HF}$ $\text{XeF}_6 + 2\text{H}_2\text{O} \longrightarrow \text{XeO}_2\text{F}_2 + 4\text{HF}$ - Action of SiO ₂ on XeOF ₄ $2\text{XeOF}_4 + \text{SiO}_2 \longrightarrow 2\text{XeO}_2\text{F}_2 + \text{SiF}_4$	- Colourless solid with melting point = 29.8°C - Undergoes hydrolysis readily $\text{XeO}_2\text{F}_2 + \text{H}_2\text{O} \longrightarrow \text{XeO}_3 + 2\text{HF}$	 (+6), XeO ₂ F ₂ Distorted trigonal bipyramidal, sp ³ d

d- and f- Block Elements

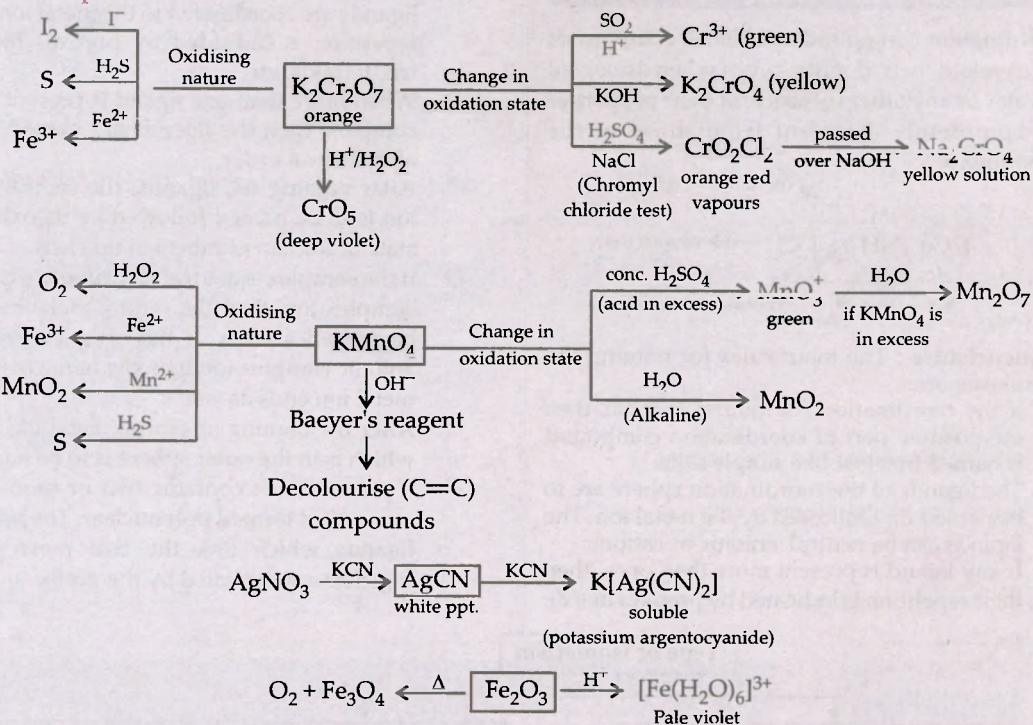
- The *d*-block elements are also called as transition elements as they show transitional properties between *s*- and *p*-block elements. These elements are called *d*-block elements since in them 3*d*, 4*d*, 5*d* and 6*d* subshells are incomplete and the last electron enters the (*n* - 1)*d* orbitals, i.e., penultimate shell. Their general electronic configuration is (*n* - 1)*d*¹⁻¹⁰ *ns*⁰⁻² where *n* is the outermost shell.

Series	Elements
First transition series or 3 <i>d</i> series	Sc (At. no. 21) to Zn (At. no. 30)
Second transition series or 4 <i>d</i> series	Y (At. no. 39) to Cd (At. no. 48)
Third transition series or 5 <i>d</i> series	La (At. no. 57), Hf (At. no. 72) to Hg (At. no. 80)
Fourth transition series or 6 <i>d</i> series	Ac (At. no. 89), Rf (At. no. 104) to Uub (At. no. 112)

Some important compounds of *d*-block elements

Compounds	Preparation	Physical properties	Uses
K ₂ Cr ₂ O ₇	From sodium dichromate (obtained from chromite ore) $\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{KCl} \longrightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl}$	Orange red, crystalline solid, oxidising agent, melting point = 398°C	in dyeing, photography, leather industry
KMnO ₄	From potassium manganate $2\text{K}_2\text{MnO}_4 + \text{Cl}_2 \longrightarrow 2\text{KMnO}_4 + 2\text{KCl}$	Dark violet, crystalline solid, oxidising agent, melting point = 523 K	as disinfectant, germicide, Baeyer's reagent (alkaline KMnO ₄)
CuSO ₄ ·5H ₂ O (blue vitriol)	From cupric oxide $\text{CuO} + \text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{H}_2\text{O}$	Blue (hydrated salt), at 423 K becomes anhydrous, readily dissolves in water	as electrolyte, mordant, fungicide
AgNO ₃ (Lunar caustic)	From silver metal $3\text{Ag} + 4\text{HNO}_3 \longrightarrow \text{AgNO}_3 + \text{NO}\uparrow + \text{H}_2\text{O}$	White crystalline, decomposes to give silver at high temperature	for making inks, hair dyes, photography, silvering of glass
HgI ₂	From mercuric chloride $\text{HgCl}_2 + 2\text{KI} \longrightarrow \text{HgI}_2 + 2\text{KCl}$	It exists in two forms, i.e., red and yellow, dissolves in excess of KI to form a complex, called as Nessler's reagent	to prepare Nessler's reagent, for making ointments for treating skin infections

Some important reactions



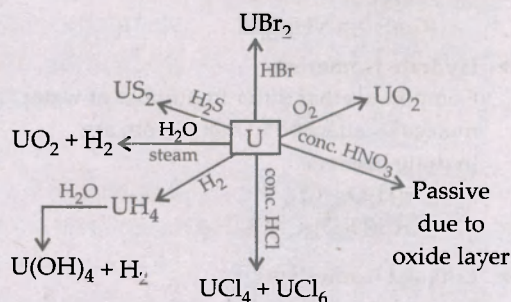
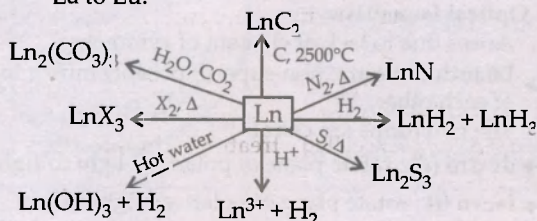
f-Block Elements

- The general electronic configuration of the *f*-block elements is $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$.
- For lanthanoid, *n* is 6 while its value is 7 for actinoid series.

Lanthanoids	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinoids	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

- (Lanthanoid contraction):** In lanthanoids there is regular decrease in atomic and ionic radii with increase in atomic number from La to Lu. This regular decrease is known as lanthanoid contraction.

○ **Cause of lanthanoid contraction :** As we move along the lanthanoid series, the nuclear charge increases by one unit at each successive element and a new electron enters the 4*f*-subshell. Due to the peculiar shape of *f*-orbitals, there is imperfection shielding of 4*f*-electrons by other electrons from the nuclear attraction. As a result of this, the size of lanthanoid atoms keep on decreasing from La to Lu.

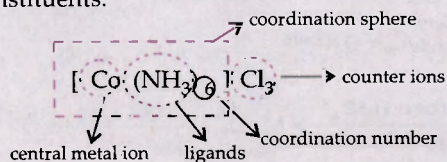


Key Points

- Actinoids form oxo-ions such as UO_2^{+} , PuO_2^{2+} , UO^+ , UO_2^+ , etc. These ions are stable in acid and aqueous solutions while lanthanoids do not form oxo-ions.
- Elements with atomic number greater than 92 (atomic number of uranium) are called transuranium elements. All these elements are man-made.

COORDINATION COMPOUNDS

- **Coordination compounds** are those compounds which retain their identities even when dissolved in water or any other solvent and their properties are completely different from those of the constituents.



- **Nomenclature** : The main rules for naming the complexes are :
 - If the coordination compound is ionic, then the positive part of coordination compound is named first just like simple salts.
 - The ligands of the coordination sphere are to be named first followed by the metal ion. The ligands can be neutral, anionic or cationic.
 - If any ligand is present more than once, then their repetition is indicated by prefixes like di,

tri, tetra, etc. When bidentate or polydentate ligands are coordinated to the metal ion, their repetition is indicated by prefixes like bis, tris, tetrakis, etc.

- When more than one ligand is present in the complex, then the ligands are named in the alphabetical order.
- After naming the ligands, the central metal ion is to be named followed by its oxidation state in Roman numbers in brackets.
- If the complex is neutral or provides a cationic complex ion, then the central metal ion is to be named as it is. If the complex provides anionic complex ion then the name of central metal ion ends as 'ate'.
- After the naming of central metal ion, anion which is in the outer sphere is to be named.
- If the complex contains two or more metal atoms, it is termed polynuclear. The bridging ligands which link the two metal atoms together are indicated by the prefix μ .

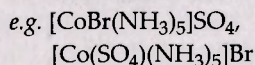
Type of Isomerism

STRUCTURAL ISOMERISM

When compounds have different ligands within their coordination spheres.

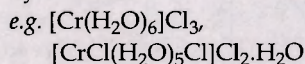
Ionisation Isomerism

Compounds that give different ions in solution are ionisation isomers.



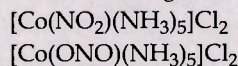
Hydrate Isomerism

Compounds that differ in number of water molecules attached to metal atom are hydrate isomers.



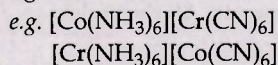
Linkage Isomerism

Shown by compounds containing ambidentate ligands.



Coordination Isomerism

Occurs when both positive and negative ions are complex ions and two isomers differ in ligand's distribution in two complex ions.



STEREoisomerism

When different positions and arrangements of ligands in space.

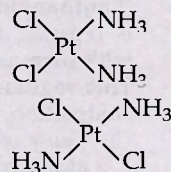
Geometrical Isomerism

Arises in heteroleptic complexes due to different possible geometric arrangements of the ligands.

In square planar complex $[\text{Ma}_2\text{b}_2]$

cis : 2 ligands *a* arranged adjacent to each other

trans : 2 ligands *a* arranged opposite to each other.



In octahedral complexes $[\text{Ma}_3\text{b}_3]$

Facial (fac): 3 donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face.

Meridional (mer) : When the positions are around the meridian of the octahedron.

Optical Isomerism

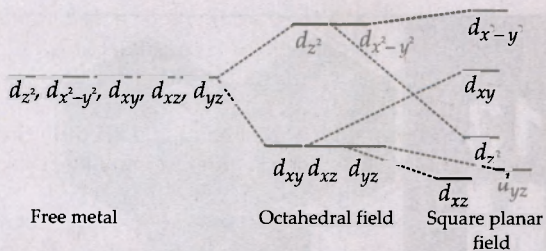
Arises due to lack of element of symmetry.

► **Enantiomers** are non-superimposable mirror image of each other.

The two forms are chiral.

► **dextro (d)** : rotate plane of polarised light to right.

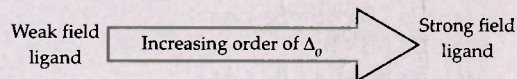
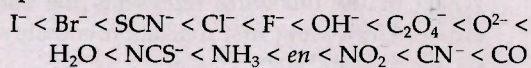
► **laevo (l)** : rotate plane of polarised light to left.



Complex	No. of 3d electrons in metal ion	Type of hybrid orbital	Geometry	No. of unpaired electrons in the complex ion
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	3	d^2sp^3	Octahedral	3
$[\text{Fe}(\text{CN})_6]^{4-}$	6	d^2sp^3	Octahedral	0
$[\text{Fe}(\text{CN})_6]^{3-}$	5	d^2sp^3	Octahedral	1
$[\text{FeF}_6]^{3-}$	5	sp^3d^2	Octahedral	5
$[\text{Co}(\text{NH}_3)_6]^{3+}$	6	d^2sp^3	Octahedral	0

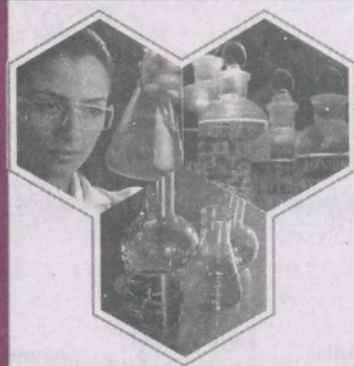
$[\text{CoF}_6]^{3-}$	6	sp^3d^2	Octahedral	4
$[\text{Ni}(\text{CN})_4]^{2-}$	8	dsp^2	Square planar	0
$[\text{Cu}(\text{NH}_3)_4]^{2+}$	9	dsp^2	Square planar	1
$[\text{Cu}(\text{CN})_4]^{3-}$	10	sp^3	Tetrahedral	0
$[\text{Mn}(\text{CN})_6]^{3-}$	4	d^2sp^3	Octahedral	2
$[\text{Mn}(\text{H}_2\text{O})_3]^{3+}$	4	sp^3d^2	Octahedral	4
$\text{Ni}(\text{CO})_4$	10	sp^3	Tetrahedral	0
$[\text{Ni}_2\text{Cl}_4]^{2-}$	8	sp^3	Tetrahedral	2

• Spectrochemical series :



Solved Paper 2013

JEE MAIN



- Which of the following represents the correct order of increasing first ionization enthalpy for Ca, Ba, S, Se and Ar?
 - Ca < Ba < S < Se < Ar
 - Ca < S < Ba < Se < Ar
 - S < Se < Ca < Ba < Ar
 - Ba < Ca < Se < S < Ar
- A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is
 - 6
 - 2
 - 5
 - 4
- Energy of an electron is given by

$$E = -2.178 \times 10^{-18} \text{ J} \left(\frac{Z^2}{n^2} \right)$$
 Wavelength of light required to excite an electron in an hydrogen atom from level $n = 1$ to $n = 2$ will be
 $(h = 6.62 \times 10^{-34} \text{ J s and } c = 3.0 \times 10^8 \text{ m s}^{-1})$
 - $8.500 \times 10^{-7} \text{ m}$
 - $1.214 \times 10^{-7} \text{ m}$
 - $2.816 \times 10^{-7} \text{ m}$
 - $6.500 \times 10^{-7} \text{ m}$
- An unknown alcohol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism?
 - tertiary alcohol by $\text{S}_{\text{N}}2$
 - secondary alcohol by $\text{S}_{\text{N}}1$
 - tertiary alcohol by $\text{S}_{\text{N}}1$
 - secondary alcohol by $\text{S}_{\text{N}}2$
- A gaseous hydrocarbon gives upon combustion 0.72 g of water and 3.08 g of CO_2 . The empirical formula of the hydrocarbon is
 - C_7H_8
 - C_2H_4
 - C_3H_4
 - C_6H_5
- A solution of (–) – 1 – chloro – 1 – phenylethane in toluene racemises slowly in the presence of a small amount of SbCl_5 , due to the formation of
 - free radical
 - carbanion
 - carbene
 - carbocation.
- Which one of the following molecules is expected to exhibit diamagnetic behaviour?
 - S_2
 - C_2
 - N_2
 - O_2
- Which of the following exists as covalent crystals in the solid state?
 - Phosphorus
 - Iodine
 - Silicon
 - Sulphur
- Given
 $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74 \text{ V}$; $E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51 \text{ V}$
 $E^\circ_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33 \text{ V}$; $E^\circ_{\text{Cl}^-/\text{Cl}_2} = 1.36 \text{ V}$
 Based on the data given above, strongest oxidising agent will be
 - MnO_4^-
 - Cl^-
 - Cr^{3+}
 - Mn^{2+}
- Arrange the following compounds in order of decreasing acidity.

(I)

(II)

(III)

(IV)

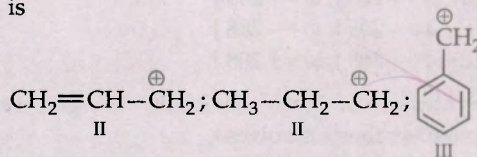
 - IV > III > I > II
 - II > IV > I > III
 - I > II > III > IV
 - III > I > II > IV
- The molarity of a solution obtained by mixing 750 mL of 0.5 M HCl with 250 mL of 2 M HCl will be
 - 0.975 M
 - 0.875 M
 - 1.00 M
 - 1.75 M
- For gaseous state, if most probable speed is denoted by C^* , average speed by \bar{C} and mean square speed by C , then for a large number of molecules the ratios of these speed are

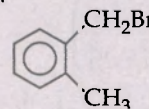
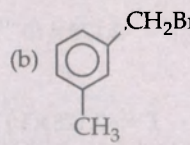
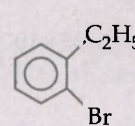
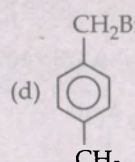
- (a) $C^* : \bar{C} : C = 1 : 1.225 : 1.128$
 (b) $C^* : \bar{C} : C = 1.225 : 1.128 : 1$
 (c) $C^* : \bar{C} : C = 1.128 : 1 : 1.225$
 (d) $C^* : \bar{C} : C = 1 : 1.128 : 1.225$
13. Which of the following is the wrong statement?
 (a) Ozone is diamagnetic gas.
 (b) ONCl and ONO^- are not isoelectronic.
 (c) O_3 molecule is bent.
 (d) Ozone is violet-black in solid state.
14. An organic compound A upon reacting with NH_3 gives B. On heating, B gives C. C in presence of KOH reacts with Br_2 to give $CH_3CH_2NH_2$. A is
 (a) CH_3CH_2COOH (b) CH_3COOH
 (c) $CH_3CH_2CH_2COOH$
 (d) $CH_3-\underset{\text{CH}_3}{\underset{|}{CH}}-COOH$
15. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest $E_{M^{3+}/M^{2+}}$ value?
 (a) Co (Z = 27) (b) Cr (Z = 24)
 (c) Mn (Z = 25) (d) Fe (Z = 26)
16. In which of the following pairs of molecules/ions, both the species are not likely to exist?
 (a) H_2, He_2^{2+} (b) H_2^+, He_2^{2-}
 (c) H_2, He_2^{2-} (d) H_2^+, He_2
17. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was
 (a) Phosgene (b) Methylisocyanate
 (c) Methylamine (d) Ammonia
18. Consider the following reaction.

$$xMnO_4 + yC_2O_4^{2-} + zH^+ \rightarrow xMn^{2+} + 2yCO_2 + \frac{z}{2}H_2O$$

 The values of x, y and z in the reaction are, respectively
 (a) 5, 2 and 8 (b) 5, 2 and 16
 (c) 2, 5 and 8 (d) 2, 5 and 16
19. Which of the following complex species is not expected to exhibit optical isomerism?
 (a) $[Co(en)(NH_3)_2Cl_2]^+$
 (b) $[Co(en)_3]^{3+}$ (c) $[Co(en)_2Cl_2]^+$
 (d) $[Co(NH_3)_3Cl_3]$
20. How many litres of water must be added to 1 litre of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2?
 (a) 9.0 L (b) 0.1 L (c) 0.9 L (d) 2.0 L

21. The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be
 ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\log 2 = 0.301$)
 (a) 60.5 kJ mol^{-1} (b) 53.6 kJ mol^{-1}
 (c) 48.6 kJ mol^{-1} (d) 58.5 kJ mol^{-1}
22. The first ionisation potential of Na is 5.1 eV. The value of electron gain enthalpy of Na^+ will be
 (a) +2.55 eV (b) -2.55 eV
 (c) -5.1 eV (d) -10.2 eV
23. The coagulating power of electrolytes having ions Na^+ , Al^{3+} and Ba^{2+} for arsenic sulphide sol increases in the order :
 (a) $Al^{3+} < Na^+ < Ba^{2+}$ (b) $Al^{3+} < Ba^{2+} < Na^+$
 (c) $Na^+ < Ba^{2+} < Al^{3+}$ (d) $Ba^{2+} < Na^+ < Al^{3+}$
24. The order of stability of the following carbocations is



- (a) III > I > II (b) III > II > I
 (c) II > III > I (d) I > II > III
25. Stability of the species Li_2 , Li_2^- and Li_2^+ increases in the order of
 (a) $Li_2^- < Li_2 < Li_2^+$ (b) $Li_2 < Li_2^- < Li_2^+$
 (c) $Li_2^- < Li_2^+ < Li_2$ (d) $Li_2 < Li_2^- < Li_2^+$
26. Compound (A), C_8H_9Br , gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A).
- (a)  (b) 
 (c)  (d) 
27. Which of the following arrangements does not represent the correct order of the property stated against it?
 (a) $Sc < Ti < Cr < Mn$: number of oxidation states
 (b) $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$: paramagnetic behaviour

- (c) $\text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{Mn}^{2+}$: ionic size
 (d) $\text{Co}^{3+} < \text{Fe}^{3+} < \text{Cr}^{3+} < \text{Sc}^{3+}$: stability in aqueous solution.

28. Experimentally it was found that a metal oxide has formula $\text{M}_{0.98}\text{O}$. Metal M , is present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M^{3+} would be

- (a) 5.08% (b) 7.01%
 (c) 4.08% (d) 6.05%

29. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C . As it does so, it absorbs 208 J of heat. The values of q and w for the process will be

($R = 8.314 \text{ J/mol K}$) ($\ln 7.5 = 2.01$)

- (a) $q = +208 \text{ J}$, $w = +208 \text{ J}$
 (b) $q = +208 \text{ J}$, $w = -208 \text{ J}$
 (c) $q = -208 \text{ J}$, $w = -208 \text{ J}$
 (d) $q = -208 \text{ J}$, $w = +208 \text{ J}$

30. Synthesis of each molecule of glucose in photosynthesis involves

- (a) 6 molecules of ATP
 (b) 18 molecules of ATP
 (c) 10 molecules of ATP
 (d) 8 molecules of ATP

SOLUTIONS

1. (d): Ionization enthalpy decreases from top to bottom in a group while it increases from left to right in a period.

2. (c): No. of amino groups = $\frac{390 - 180}{42} = 5$

3. (b): $E = -2.178 \times 10^{-18} \text{ Z}^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

$$E = -2.178 \times 10^{-18} \left[\frac{1}{(2)^2} - \frac{1}{(1)^2} \right]$$

$$E = +2.178 \times 10^{-18} \times \frac{3}{4} = 1.6335 \times 10^{-18} \text{ J}$$

$$E = \frac{hc}{\lambda}$$

$$\Rightarrow \lambda = \frac{hc}{E} = \frac{6.62 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ m}}{1.6335 \times 10^{-18} \text{ J}}$$

$$\lambda = 12.14 \times 10^{-8} \text{ m}$$

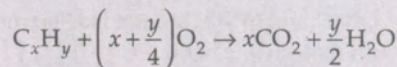
$$\text{or } \lambda = 1.214 \times 10^{-7} \text{ m}$$

4. (c): In Lucas test, turbidity appears immediately with tertiary alcohol by $\text{S}_{\text{N}}1$ mechanism.

5. (a): Moles of water produced = $\frac{0.72}{18} = 0.04$

$$\text{Moles of } \text{CO}_2 \text{ produced} = \frac{3.08}{44} = 0.07$$

Equation for combustion of an unknown hydrocarbon, C_xH_y is



$$\Rightarrow x = 0.07$$

$$\text{and } \frac{y}{2} = 0.04$$

$$\therefore y = 0.08$$

$$\frac{x}{y} = \frac{0.07}{0.08} = \frac{7}{8}$$

\therefore The empirical formula of the hydrocarbon is C_7H_8 .

6. (d): A carbocation intermediate is formed during racemisation.

7. (d): O_2 is expected to be diamagnetic in nature but actually it is paramagnetic.

8. (c)

9. (a): Greater the reduction potential of a substance, stronger is the oxidising agent.

$\therefore \text{MnO}_4^-$ is the strongest oxidising agent.

10. (d): Electron donating groups ($-\text{CH}_3$ and $-\text{OCH}_3$) decrease while electron withdrawing groups ($-\text{NO}_2$ and $-\text{Cl}$) increase the acidity.

Since $-\text{OCH}_3$ is a stronger electron donating group than $-\text{CH}_3$ and $-\text{NO}_2$ is stronger electron withdrawing group than $-\text{Cl}$, therefore order of decreasing acidity is $\text{III} > \text{I} > \text{II} > \text{IV}$.

11. (b): $M_{\text{mix}} V_{\text{mix}} = M_1 V_1 + M_2 V_2$

$$M_{\text{mix}} = \frac{M_1 V_1 + M_2 V_2}{V_{\text{mix}}}$$

$$M_{\text{mix}} = \frac{0.5 \times 750 + 2 \times 250}{1000}$$

$$M_{\text{mix}} = 0.875 \text{ M}$$

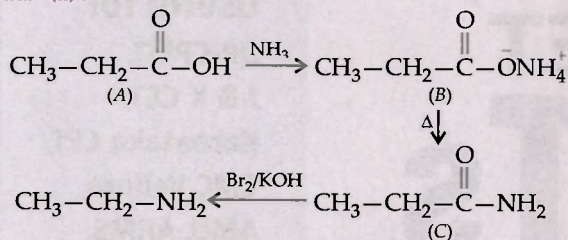
12. (d): $\text{C}^* : \text{C} : \text{C} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{3RT}{M}}$

$$= \sqrt{2} : \sqrt{\frac{8}{3.14}} = \sqrt{3}$$

$$\therefore \text{C}^* : \text{C} : \text{C} = 1 : 1.128 : 1.225$$

13. (None): All the statements are correct.

14. (a):



15. (a)

16. (d): Species with zero bond order does not exist.

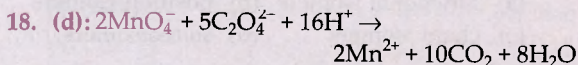
$$\text{H}_2^{2+} : \sigma(1s)^0$$

$$\therefore \text{Bond order} = 0$$

$$\text{He}_2 : \sigma(1s)^2 \sigma^*(1s)^2$$

$$\text{Bond order} = \frac{2-2}{2} = 0$$

17. (b)



$$\therefore x = 2, y = 5, z = 16$$

19. (d): $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ will not exhibit optical isomerism due to presence of plane of symmetry.

20. (a): Initial concentration of aq. HCl solution with pH 1 = 10^{-1} M

Final concentration of this solution after dilution = 10^{-2} M

$$MV = M_1(V_1 + V_2)$$

$$10^{-1} \times 1 = 10^{-2} (1 + V)$$

$$\frac{0.1}{0.01} = 1 + V$$

$$10 = 1 + V$$

$$\Rightarrow V = 9 \text{ L}$$

21. (b): As $r = k[A]^n$

$$\frac{r_2}{r_1} = \frac{k_2}{k_1}$$

Since $\frac{r_2}{r_1} = 2$ (Given)

$$\therefore \frac{k_2}{k_1} = 2$$

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314 \times 10^{-3}} \left[\frac{310 - 300}{310 \times 300} \right]$$

$$E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 10^{-3} \times 93 \times 10^3}{10}$$

$$E_a = 53.6 \text{ kJ mol}^{-1}$$

22. (c): Electron gain enthalpy = - Ionisation potential
= - 5.1 eV

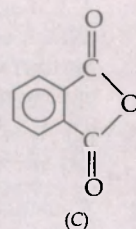
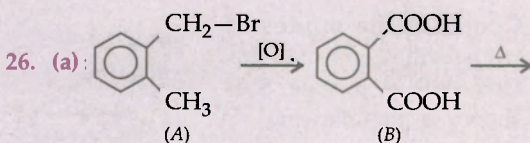
23. (c): For a negatively charged sol, like As_2S_3 , greater the positive charge on cations, greater is the coagulating power.

24. (a): Greater the number of resonating structures a carbocation possess, greater is its stability.

25. (c): Species Bond order

Li_2	1
Li_2^+	0.5
Li_2^-	0.5

Higher the bond order, greater is the stability.



27. (b): Number of unpaired electrons in Fe^{2+} is less than Mn^{2+} , so Fe^{2+} is less paramagnetic than Mn^{2+} .

28. (c): Let the fraction of metal which exists as M^{3+} be x .

Then the fraction of metal as $M^{2+} = (0.98 - x)$

$$\therefore 3x + 2(0.98 - x) = 2$$

$$x + 1.96 = 2$$

$$x = 0.04$$

$$\therefore \% \text{ of } M^{3+} = \frac{0.04}{0.98} \times 100 = 4.08\%$$

29. (b): As it absorbs heat,

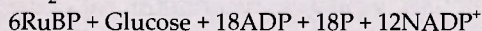
$$\therefore q = +208 \text{ J}$$

$$W_{rev} = -2.303 nRT \log_{10} \left(\frac{V_2}{V_1} \right)$$

$$W_{rev} = -2.303 \times (0.04) \times 8.314 \times 310 \log_{10} \left(\frac{375}{50} \right)$$

$$\therefore W_{rev} = -207.76 \approx -208 \text{ J}$$

30. (b): $6\text{CO}_2 + 18\text{ATP} + 12\text{NADPH} + 6\text{RuBP} \rightarrow$



One molecule of glucose is formed from 6CO_2 by utilising 18ATP and 12NADPH.

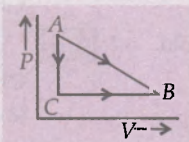


TARGET PMTs

PRACTICE QUESTIONS

Useful for
UP-CPMT,
J & K CET,
Karnataka CET,
CMC Vellore,
AMU, AIIMS,
WB JEE,
MGM CET

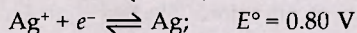
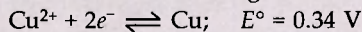
1. Consider the modes of transformations of a gas from state 'A' to state 'B' as shown in the following P-V diagram.



Which one of the following is true ?

- (a) $\Delta H = q$ along $A \rightarrow C$
(b) ΔS is same along both $A \rightarrow B$ and $A \rightarrow C \rightarrow B$
(c) w is same along both $A \rightarrow B$ and $A \rightarrow C \rightarrow B$
(d) $w > 0$ along both $A \rightarrow B$ and $A \rightarrow C$.

2. Consider the following half cell reactions.



Which one of the following is true?

- (a) Copper can displace silver from AgNO_3 solution.
(b) Silver can displace copper from $\text{Cu}(\text{NO}_3)_2$ solution.
(c) Silver is more reactive than copper.
(d) Cu^{2+}/Cu and Ag^+/Ag with positive E° values cannot be coupled to form a Galvanic cell.

3. If a 0.00001 molar solution of HCl is diluted thousand folds the pH of the resulting solution will be

- (a) 5
(b) 7
(c) 8
(d) 6.98

4. If 100 g iron powder (at. wt. of Fe = 56) is heated with 32 g of sulphur (at. wt. of S = 32). To prepare one mole of iron sulphide how much iron powder will remain unreacted?

- (a) 4 g
(b) 32 g
(c) 44 g
(d) Nil

5. A primary alcohol, $\text{C}_3\text{H}_8\text{O}$ (P) on heating with sulphuric acid undergoes dehydration to give an

alkene, Q, which reacts with HCl to give R. R on treatment with aqueous KOH gives compound S, $\text{C}_3\text{H}_8\text{O}$. P and S are

- (a) functional isomers (b) position isomers
(c) chain isomers (d) stereoisomers.

6. The aqueous solution of which of the following salt will have the lowest pH?

- (a) NaClO_3 (b) NaClO
(c) NaClO_4 (d) NaClO_2

7. In the reaction: $\text{P}_2\text{O}_5 + 2\text{HNO}_3 \rightarrow 2\text{HPO}_3 + x$, the term x is

- (a) N_2O_4 (b) H_2O
(c) N_2O_5 (d) PNO_3

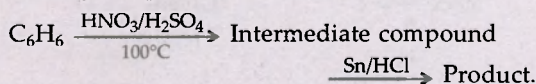
8. In the reaction: $\text{I}_2 + \text{I}^- \rightarrow \text{I}_3^-$, the Lewis base is

- (a) I^- (b) I_2
(c) I_3^- (d) none of these.

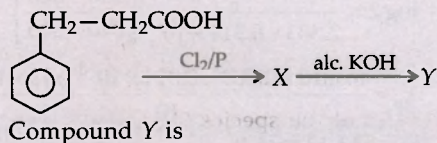
9. The correct order of the increasing ionic character is

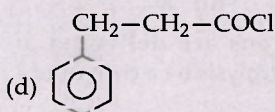
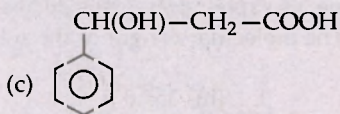
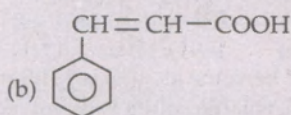
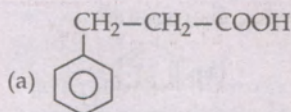
- (a) $\text{BeCl}_2 < \text{MgCl}_2 < \text{BaCl}_2 < \text{CaCl}_2$
(b) $\text{BeCl}_2 < \text{MgCl}_2 < \text{CaCl}_2 < \text{BaCl}_2$
(c) $\text{BeCl}_2 < \text{BaCl}_2 < \text{MgCl}_2 < \text{CaCl}_2$
(d) $\text{BaCl}_2 < \text{CaCl}_2 < \text{MgCl}_2 < \text{BeCl}_2$

10. Identify the product in the reaction.



- (a) $\text{C}_6\text{H}_5\text{NO}_2$ (b) $\text{C}_6\text{H}_4(\text{NO}_2)_2$
(c) C_6H_4 with NO_2 and NH_2 groups (d) C_6H_4 with two NH_2 groups





12. When calcium acetate and calcium formate together are subjected to dry distillation, the product is

- (a) acetaldehyde (b) acetone
(c) formaldehyde (d) none of these.

13. At 27°C a gas was compressed to half of its volume. To what temperature must it now be heated so that it occupies its original volume?

- (a) 54°C (b) 327°C
(c) 600°C (d) 327 K

14. The oxide that gives hydrogen peroxide on treatment with a dilute acid is

- (a) PbO₂ (b) Na₂O₂
(c) MnO₂ (d) TiO₂

15. Relative acidity of the following is in the order

- (a) RCOOH > H₂CO₃ > C₆H₅OH > H₂O > ROH
(b) RCOOH > ROH > H₂CO₃ > C₆H₅OH > H₂O
(c) ROH > RCOOH > H₂CO₃ > C₆H₅OH > H₂O
(d) RCOOH > C₆H₅OH > ROH > H₂CO₃ > H₂O

16. Which one of the following is not coloured?

- (a) Cu²⁺ (b) Cu⁺
(c) Ni²⁺ (d) Fe³⁺

17. Which one of the following is incorrect?

- (a) Boron halides are all monomeric while those of Al are dimeric.
(b) Boron halides and aluminium halides exist as monomeric halides.
(c) Boron halides and aluminium halides are Lewis acids.
(d) B₂O₃ alone is acidic while Al₂O₃ is amphoteric.

18. Bond order of the species O₂, O₂⁺, O₂²⁺ and O₂⁻ increases in the order

- (a) O₂ < O₂⁻ < O₂²⁺ < O₂⁺
(b) O₂⁻ < O₂ < O₂⁺ < O₂²⁺
(c) O₂ < O₂²⁺ < O₂ < O₂⁻
(d) O₂²⁺ < O₂⁺ < O₂ < O₂⁻

19. A compound formed by elements K and L crystallises in the cubic arrangement in which K atoms are at the corners of a cube and L atoms are at the face centres. What is the formula of compound?

- (a) KL₃ (b) L₃K
(c) K₂L₂ (d) KL₂

20. Which of the following will exhibit highest boiling point?

- (a) CH₃CH₂OCH₂CH₂CH₃
(b) CH₃CH₂CH₂CH₂CH₂OH
(c) CH₃CH₂CH₂CH(CH₃)OH
(d) CH₃CH₂C(CH₃)₂OH

21. The amine which can react with C₆H₅SO₂Cl to form a product insoluble in alkali shall be

- (a) a primary amine
(b) a secondary amine
(c) a tertiary amine
(d) both primary and secondary amines.

22. Addition of conc. HCl to saturated BaCl₂ solution precipitates BaCl₂ because

- (a) it follows Le Chatelier's principle
(b) of common ion effect
(c) ionic product [Ba²⁺][Cl⁻] remains constant in a saturated solution
(d) at constant temperature, the product [Ba²⁺][Cl⁻]² remains constant in a saturated solution

23. KMnO₄ acts as an oxidising agent in the neutral medium and gets reduced to MnO₂. The equivalent weight of KMnO₄ in neutral medium will be

- (a) mol. wt./2 (b) mol. wt./3
(c) mol. wt./4 (d) mol. wt./7

24. Which one has the highest paramagnetism?

- (a) Ni(CO)₄ (b) [Co(NH₃)₆]Cl₃
(c) [Ni(NH₃)₆]Cl₂ (d) [Cu(NH₃)₄]Cl₂

25. The wavelength of radiation emitted when an electron in a hydrogen atom makes a transition from an energy level with $n = 3$ to a level with $n = 2$ is

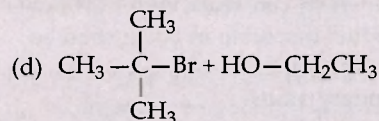
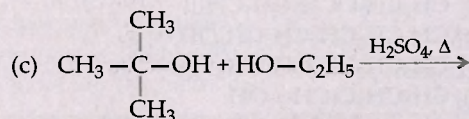
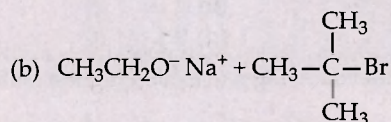
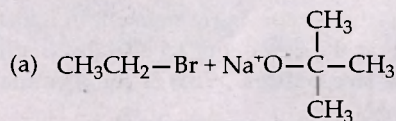
[Given that $E_n = \frac{-1312}{n^2} \text{ kJ mol}^{-1}$]

- (a) $6.56 \times 10^{-7} \text{ m}$ (b) 65.6 nm
(c) $65.6 \times 10^{-7} \text{ m}$ (d) None of these.

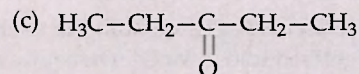
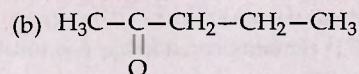
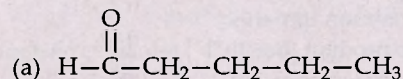
26. Which of the following solutions boils at the highest temperature?

- (a) 0.1 M Glucose (b) 0.1 M NaCl
(c) 0.1 M BaCl₂ (d) 0.1 M Urea

27. For the preparation of *t*-butyl ethyl ether, which method/reaction is to be preferred?



28. Compound *P* (C₅H₁₀O) forms phenyl hydrazone and gives a negative Tollen's and iodoform test. Compound *P* on reduction gives *n*-pentane. The compound *P* will be

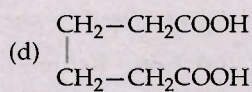
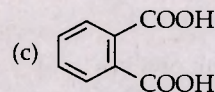
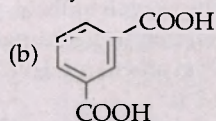
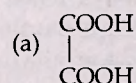


(d) None of the above.

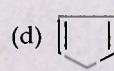
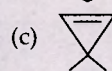
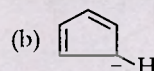
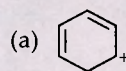
29. Which of the following is an amphoteric oxide?

- (a) CrO₃ (b) Cr₂O₃
(c) V₂O₃ (d) TiO

30. Among the following acids, the one which can form an anhydride most easily is



31. Which of the following is aromatic?



32. Vapour pressure of benzene at 30°C is 121.8 mm. When 15 g of a non-volatile solute is dissolved in 250 g of benzene, its vapour pressure is decreased to 120.2 mm. The molecular weight of the solute is

- (a) 35.67 g (b) 357.8 g
(c) 432.8 g (d) 502.7 g

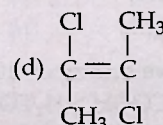
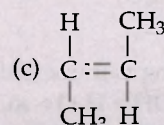
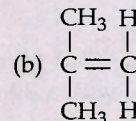
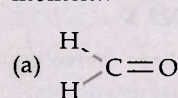
33. How many electrons are delivered at the cathode during electrolysis by a current of 1 A in 60 seconds?

- (a) 3.74×10^{20} (b) 6.0×10^{23}
(c) 7.48×10^{21} (d) 6.0×10^{20}

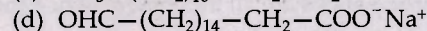
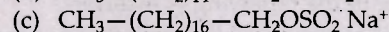
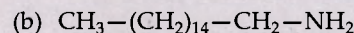
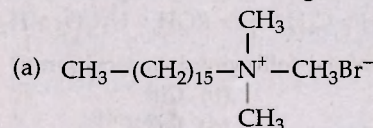
34. The heat of neutralization of a strong base and a strong acid is 57 kJ. The heat released when 0.5 mole of HNO₃ solution is added to 0.20 mole of NaOH solution, is

- (a) 11.4 kJ (b) 34.7 kJ
(c) 23.5 kJ (d) 58.8 kJ

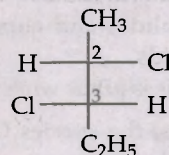
35. Which of the following has the highest dipole moment?



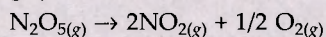
36. Which one of the following is not a surfactant?



37. The absolute configuration of the following compound is



- (a) 2S, 3R (b) 2S, 3S
(c) 2R, 3S (d) 2R, 3R
38. The treatment of benzene with *iso*-butene in the presence of sulphuric acid gives
(a) *iso*-butylbenzene (b) *tert*-butylbenzene
(c) *n*-butylbenzene (d) no reaction.
39. Which of the following can exhibit geometrical isomersim?
(a) $[\text{MnBr}_4]^{2-}$
(b) $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$
(c) $[\text{PtCl}_2\cdot\text{P}(\text{C}_2\text{H}_5)_3]_2$
(d) None of these
40. The ONO angle is maximum in
(a) NO_3^- (b) NO_2^-
(c) NO_2 (d) NO_2^+
41. The rate constant k , for the given reaction is $2.3 \times 10^{-2} \text{ s}^{-1}$.



Which equation given below describes the change of $[\text{N}_2\text{O}_5]$ with time? $[\text{N}_2\text{O}_5]_0$ and $[\text{N}_2\text{O}_5]_t$ correspond to concentration of N_2O_5 initially and at time t .

- (a) $[\text{N}_2\text{O}_5]_t = [\text{N}_2\text{O}_5]_0 + kt$
(b) $[\text{N}_2\text{O}_5]_0 = [\text{N}_2\text{O}_5]_t e^{kt}$
(c) $\log[\text{N}_2\text{O}_5]_t = \log[\text{N}_2\text{O}_5]_0 + kt$
(d) $\ln \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t} = kt$
42. The two-third life ($t_{2/3}$) of a first order reaction in which $k = 5.48 \times 10^{-14} \text{ s}^{-1}$ is
(a) $\frac{2.303}{5.48 \times 10^{-14}} \log 3$ (b) $\frac{2.303}{5.48 \times 10^{-14}} \log 2$
(c) $\frac{2.303}{5.48 \times 10^{-14}} \log \frac{1}{3}$ (d) $\frac{2.303}{5.48 \times 10^{-14}} \log \frac{2}{3}$
43. At what temperature the *r.m.s* velocity of chlorine gas will be equal to that of SO_2 at STP?
(a) 57.59°C (b) 0°C
(c) 273°C (d) 302.9°C
44. Which of the following ions has the greatest coagulating power when added to negative As_2S_3 sol?
(a) Na^+ (b) Mg^{2+} (c) Al^{3+} (d) PO_4^{3-}
45. Insulin contains about 0.08% by weight of sulphur. What would be the approximate molecular mass of insulin if one sulphur atom is present in a molecule of insulin?
(a) 40,000 (b) 2560
(c) 20,000 (d) 25,600

46. If the concentration of CrO_4^{2-} ions in a saturated solution of silver chromate is $2 \times 10^{-4} \text{ M}$, what is the solubility product of silver chromate?
(a) 4×10^{-8} (b) 8×10^{-12}
(c) 16×10^{-12} (d) 32×10^{-12}
47. Which is correct statement among the following?
(a) Starch is a polymer of α -glucose.
(b) Amylose is a component of cellulose.
(c) Proteins are compounds of only one type of amino acid.
(d) In cyclic structure of fructose, there are four carbon and one oxygen atom.
48. For the square planar complex, $[\text{M}(\text{A})(\text{B})(\text{C})(\text{D})]$ (where, M = central metal; A , B , C and D are monodentate ligands) the number of possible geometrical isomers are
(a) 1 (b) 2
(c) 3 (d) 4
49. During electrolysis of water the volume of O_2 liberated is 2.24 dm^3 . The volume of hydrogen liberated, under same conditions will be
(a) 2.24 dm^3 (b) 1.12 dm^3
(c) 4.48 dm^3 (d) 0.56 dm^3
50. In an isothermal process,
(a) $q = 0$ and $\Delta E = 0$ (b) $q \neq 0$ and $\Delta E = 0$
(c) $q = 0$ and $\Delta E \neq 0$ (d) $q \neq 0$ and $\Delta E \neq 0$

SOLUTIONS

1. (b) : Entropy is a state function *i.e.* the change in entropy depends upon the initial and final states of the system and not on how that change is brought about.
2. (a) : The silver electrode has higher reduction potential. The resulting galvanic cell is
$$\text{Cu}_{(s)} | \text{Cu}^{2+}_{(aq)} || \text{Ag}^{+}_{(aq)} | \text{Ag}$$
3. (d) : For 0.00001 M HCl , $[\text{H}^+] = 10^{-5} \text{ M}$.

When HCl is diluted thousand fold, $[\text{H}^+] = 10^{-8} \text{ M}$

Dissociation of water, $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$

Conc. if no dissociation C 10⁻⁸ 0

Conc. after dissociation C - x (10⁻⁸ + x) x

$$K_w = 10^{-14} = (10^{-8} + x) \times x$$

$$\Rightarrow x^2 + 10^{-8}x - 10^{-14} = 0$$

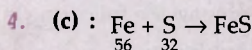
$$\Rightarrow x = 9.5 \times 10^{-8} \text{ [neglecting the -ve root]}$$

$$x = [\text{OH}^-] = 9.5 \times 10^{-8} \text{ mol dm}^{-3}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{9.5 \times 10^{-8}}$$

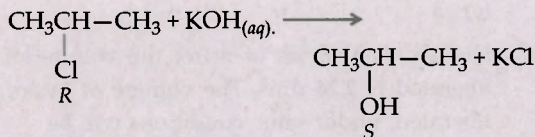
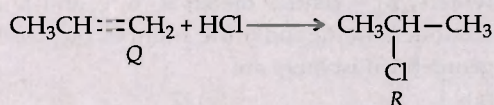
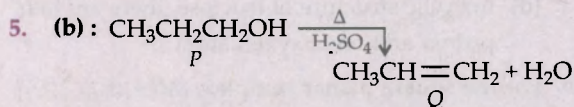
$$[\text{H}^+] = 1.005 \times 10^{-7} \text{ mol dm}^{-3}$$

$$\therefore \text{pH} = -\log[\text{H}^+] = 6.99$$



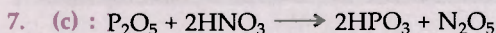
32 g of S and 56 g of Fe is required to prepare one mole of FeS.

$\therefore 100 - 56 = 44$ g of iron powder will remain unreacted.

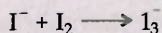


P and S are position isomers.

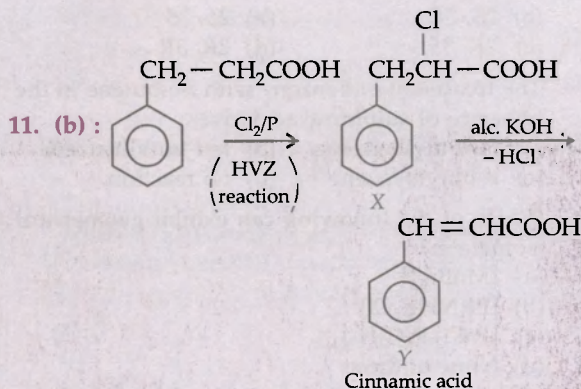
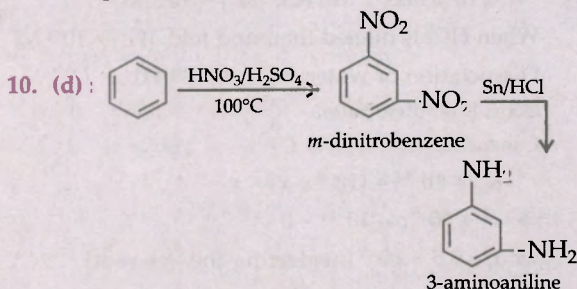
6. (c) : NaClO_4 on hydrolysis, gives strongest acid HClO_4 as compared to other salts. This is strongly ionized and gives highest concentration of H^+ . Therefore aqueous solution of NaClO_4 will have lowest pH value.



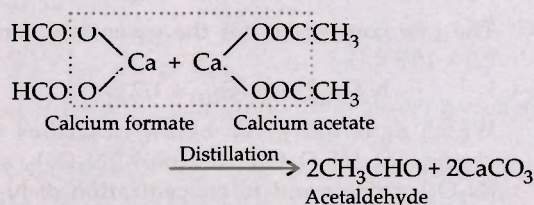
8. (a) : I^- ion can act as Lewis base *i.e.* it can donate electron pair to some species *e.g.* I_2 . The electron donor species are termed as Lewis base.



9. (b) : In the alkaline earth metal group, down the group as the size increases the ionic character of compound increases.



12. (a) : When calcium formate is distilled with calcium acetate, acetaldehyde is formed.



13. (b) : Given that $T_1 = 273 + 27 = 300 \text{ K}$

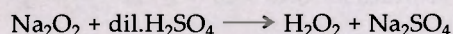
Let original volume of gas = $V = V_2$

$$\therefore V_1 = V/2$$

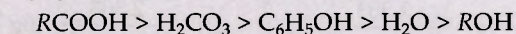
$$V_1/T_1 = V_2/T_2 \Rightarrow V/2/300 = V/T_2$$

$$\therefore T_2 = 600 \text{ K or } 327^\circ\text{C}$$

14. (b) : Sodium peroxide gives hydrogen peroxide on treatment with dil. acid.



15. (a) : The order of acidity of RCOOH , H_2CO_3 , $\text{C}_6\text{H}_5\text{OH}$, H_2O , and ROH is

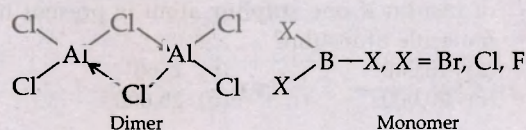


Increasing K_a value

Increasing acidic strength

16. (b) : Cu^+ has $3d^{10}$ outer electronic configuration (completely filled *d*-orbital) with zero unpaired electrons, as a result *d-d* transitions (responsible for absorption of light radiation and hence imparting colour) are not possible. Thus compounds of Cu^+ are colourless.

17. (b) : Trihalides of boron are monomeric, whereas halides of Al like AlCl_3 exist as dimers, Al_2Cl_6 .



$$18. (b) : O_2 = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2$$

$$\pi 2p_x^2 \approx \pi 2p_y^2 \quad \pi^* 2p_x^1 \approx \pi^* 2p_y^1$$

$$B.O. = \frac{1}{2} (10 - 6) = 2$$

Similarly B.O. for :

$$O_2^+ = 2.5, O_2^{2+} = 3, O_2^{2-} = 1$$

Hence, the increasing order of bond order is

$$O_2^{2-} < O_2 < O_2^+ < O_2^{2+}$$

$$19. (a) : \text{No. of K atoms} = \frac{1}{8} \times 8 = 1 \quad (\text{At corners})$$

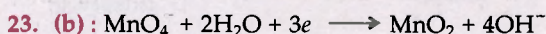
$$\text{No. of L atoms} = \frac{1}{2} \times 6 = 3 \quad (\text{Face centres})$$

\therefore Formula of the compound is KL_3 .

20. (b) : Boiling point of alcohols is higher than ethers due to H-bonding. In alcohols, the boiling point decreases with branching due to decrease in surface area. Hence, *n*-pentanol will have highest boiling point.

21. (b) : Secondary amine when reacts with $C_6H_5SO_2Cl$ (Hinsberg's reagent) forms dialkyl sulphonamide which does not dissolve in alkali.

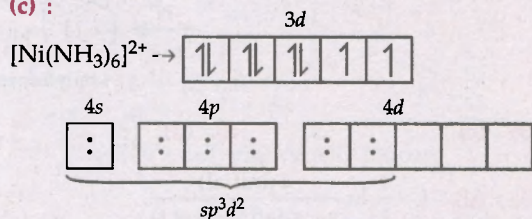
22. (b)



$$\text{Equivalent mass} = \frac{\text{Molecular mass}}{3}$$

$$= \frac{158}{3} = 52.66$$

24. (c) :



Options (a) and (b) have zero unpaired electron.

Option (d) has one unpaired electron.

$$25. (a) : \Delta E = \frac{hc}{\lambda} = E_3 - E_2 = \frac{-1312}{3^2} + \frac{1312}{2^2}$$

$$= \frac{-5248 + 11808}{36}$$

$$\Delta E = 182.2 \text{ kJ mol}^{-1} = \frac{182.2 \times 10^3}{6 \times 10^{23}} \text{ J atom}^{-1}$$

$$\Rightarrow \lambda = \frac{hc \times 6 \times 10^{23}}{182.2 \times 10^3}$$

$$= \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{182.2 \times 10^3} \times 6 \times 10^{23}$$

$$= 0.652 \times 10^{-6} \text{ m} = 6.52 \times 10^{-7} \text{ m}$$

26. (c) : van't Hoff factor for $BaCl_2$ (= 3) is highest among given solutes.

27. (a)

28. (c) : $P(C_5H_{10}O) \longrightarrow$ formation of phenyl hydrazone

i.e. *P* must be a carbonyl compound.

P \longrightarrow negative Tollen's test,

i.e. It must be a ketone.

P \longrightarrow no iodoform test

i.e. *P* does not contain CH_3CO - group.

P must be $H_3CCH_2-CO-CH_2CH_3$.

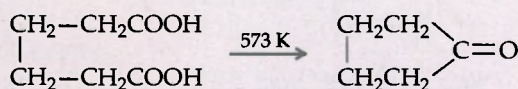
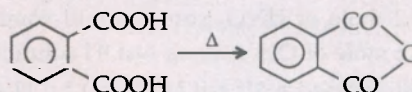
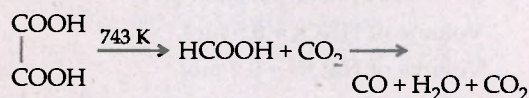
29. (b) : Cr_2O_3 is an amphoteric oxide.

CrO_3 is an acidic oxide.

V_2O_3 is basic oxide.

TiO is basic oxide.

30. (c) : The effect of heat on dicarboxylic acids can be summarised in the form of Blanc's rule which states that dicarboxylic acids in which the two carboxyl groups are attached to the same carbon atom on heating undergo decarboxylation to form monocarboxylic acids; 1,4- and 1,5- dicarboxylic acids on heating alone or distillation with acetic anhydride form cyclic anhydrides while 1,6- and 1,7- dicarboxylic acids on heating alone or on distillation with acetic anhydride give cyclic ketones with loss of one carbon atom as carbon dioxide.



31. (b) : Aromaticity can be predicted by the use of Huckel's rule which says

- (i) $(4n + 2) \pi$ -electrons are required in delocalised system to give it aromaticity.
 (ii) There must be conjugation in the species.
 (iii) The molecule must be planar.



$(4n + 2)\pi$ electrons means 2, 6, 10 ... π electrons.
 Here, total number of electrons available for delocalisation = 6

\therefore It is expected to be aromatic.

32. (b) : Relative lowering of vapour pressure is given by

$$\frac{P^0 - P}{P^0} = \frac{w/m}{w/m + W/M}$$

Where, P^0 = Vapour pressure of pure solvent

P = Vapour pressure of solution

w = Mass of solute

m = Molecular mass of solute

W = Mass of solvent

M = Molecular mass of solvent.

For dilute solution

$$\Rightarrow \frac{121.8 - 120.2}{121.8} = \frac{15/m}{250/78} \Rightarrow m = 357.8$$

33. (a) : Charge = current \times time

$$\text{Charge, } Q = 1 \text{ A} \times 60 \text{ s} \\ = 60 \text{ C}$$

Now, 96500 C charge is carried by 6.023×10^{23} electrons.

$$\Rightarrow 60 \text{ C charge} = \frac{6.023 \times 10^{23}}{96500} \times 60 \text{ electrons} \\ = 3.74 \times 10^{20} \text{ electrons}$$

34. (a) : Heat of neutralization (ΔH) = 57 kJ

Volume of HNO_3 = 0.5 mol

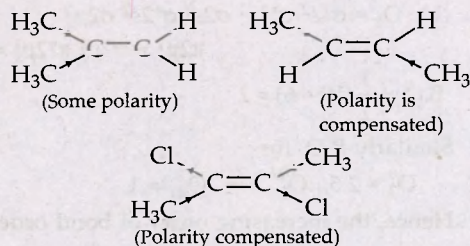
Volume of NaOH = 0.2 mol

When HNO_3 solution is added to NaOH solution, then 0.2 mole of HNO_3 solution will combine with 0.2 mole of OH^- ions of NaOH solution.

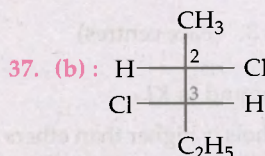
$$\therefore \text{Heat released} = \Delta H \times 0.2 = 57 \times 0.2 = 11.4 \text{ kJ}$$

35. (a) : $\text{H}-\text{C}\equiv\text{O}$

The electronegative oxygen atom is a strong electron withdrawing group. So there is polarity in the carbonyl compounds. This polarity is even greater than in the asymmetric alkene.



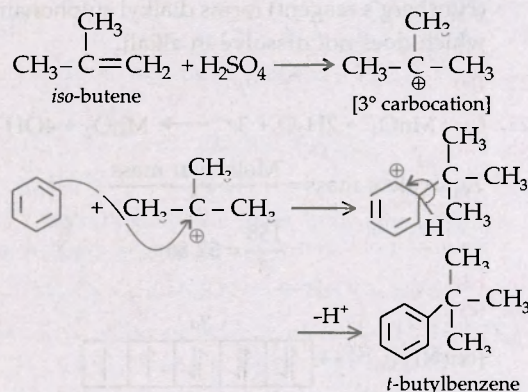
36. (b) : To act as surfactant, there should be both polar and non-polar ends in the molecules.



37. (b) :

Nomenclature is according to Cahn-Ingold-Prelog method *i.e.*, priority rule.

38. (b) :



39. (c)

40. (d)

$$41. (d) : k = \frac{1}{t} \ln \frac{a(\text{initial})}{a-x(\text{after time } t)}$$

$$k \times t = \ln \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t}$$

42. (a) : For a first order reaction,

$$k = \frac{2.303}{t_{2/3}} \log \frac{a}{a-x}$$

$$\therefore t_{2/3} = \frac{2.303}{5.48 \times 10^{-14}} \log \frac{1}{1-2/3}$$

$$t_{2/3} = \frac{2.303}{5.48 \times 10^{-14}} \log 3$$

43. (a) : $r.m.s$ velocity $= \sqrt{\frac{3RT}{M}}$

$$\Rightarrow \sqrt{\frac{3RT}{M_{Cl_2}}} = \sqrt{\frac{3R \times 298}{M_{SO_2}}} \quad (\text{at STP, } T = 298 \text{ K})$$

$$\Rightarrow \frac{T}{M_{Cl_2}} = \frac{298}{M_{SO_2}}$$

$$\Rightarrow T = \frac{298}{64} \times 71 = 330.59 \text{ K}$$

$$\Rightarrow T = 330.59 - 273$$

$$T = 57.59^\circ\text{C} \quad (\because 273 \text{ K} = 0^\circ\text{C})$$

44. (c) : According to Hardy-Schulze rule –

(i) Ions carrying charge opposite to that of the sol are effective in causing coagulation of the sol.

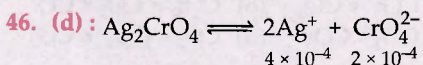
(ii) Coagulating power of an electrolyte is directly proportional to the valency of the active ions (*i.e.*, ions causing coagulation).

Since As_2S_3 is a negative sol, thus PO_4^{3-} is ineffective in causing coagulation, and out of the cations, Al^{3+} has the maximum coagulating power.

45. (a) : 0.08 g of S is present in 100 g insulin.

$$32 \text{ g of S in present in } \frac{100}{0.08} \times 32 = 40,000$$

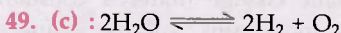
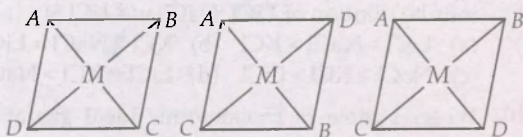
Hence, molecular mass of insulin is 40,000 g.



$$\begin{aligned} K_{sp} &= [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] \\ &= [4 \times 10^{-4}]^2 [2 \times 10^{-4}] \\ &= 32 \times 10^{-12} \end{aligned}$$

47. (a) : Starch is a polymer of α -D-glucose.

48. (c) :



Volume of H_2 and O_2 is liberated in the ratio of 2 : 1.

Hence if the volume of O_2 liberated = 2.24 dm^3 , the volume of H_2 liberated = 4.48 dm^3 .

50. (b) : For an isothermal process, $\Delta T = 0$

Hence, $\Delta E = 0$, $q \neq 0$.



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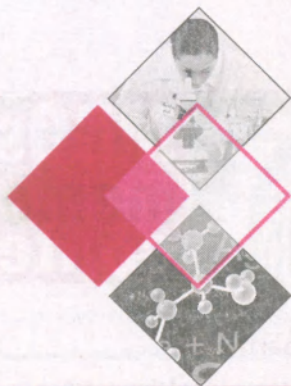
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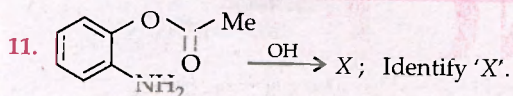
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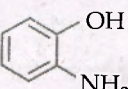
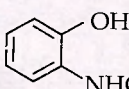
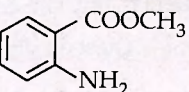
GENERAL, PHYSICAL AND INORGANIC CHEMISTRY

- The correct decreasing order of first ionisation enthalpies of five elements in the second period is
(a) $\text{Be} > \text{B} > \text{C} > \text{N} > \text{F}$ (b) $\text{N} > \text{F} > \text{C} > \text{B} > \text{Be}$
(c) $\text{F} > \text{N} > \text{C} > \text{Be} > \text{B}$ (d) $\text{N} > \text{F} > \text{B} > \text{C} > \text{Be}$
- The bonds present in the structure of dichromate ion are
(a) six equivalent $\text{Cr}-\text{O}$ bonds and one $\text{Cr}-\text{O}-\text{Cr}$ bond
(b) six equivalent $\text{Cr}-\text{O}$ bonds and one $\text{Cr}-\text{Cr}$ bond
(c) six equivalent $\text{Cr}-\text{O}$ bonds and one $\text{O}-\text{O}$ bond
(d) none of these.
- $\text{X} + \text{K}_2\text{CO}_3 + \text{air} \xrightarrow{\text{heat}} \text{Y}$; $\text{Y} + \text{Cl}_2 \longrightarrow \text{Z}$ (Pink)
which of the following is correct?
(a) $\text{X} = \text{Black, MnO}_2$; $\text{Y} = \text{Blue, K}_2\text{CrO}_4$, $\text{Z} = \text{KMnO}_4$
(b) $\text{X} = \text{Green, Cr}_2\text{O}_3$; $\text{Y} = \text{Yellow, K}_2\text{CrO}_4$, $\text{Z} = \text{K}_2\text{Cr}_2\text{O}_7$
(c) $\text{X} = \text{Black, MnO}_2$; $\text{Y} = \text{Green, K}_2\text{MnO}_4$, $\text{Z} = \text{KMnO}_4$
(d) $\text{X} = \text{Black, Bi}_2\text{O}_3$; $\text{Y} = \text{Colourless, KBiO}_4$, $\text{Z} = \text{KBiO}_3$
- The correct order of increasing bond length of F_2 , N_2 , Cl_2 and O_2 is
(a) $\text{O}_2 < \text{N}_2 < \text{Cl}_2 < \text{F}_2$ (b) $\text{N}_2 < \text{O}_2 < \text{F}_2 < \text{Cl}_2$
(c) $\text{Cl}_2 < \text{O}_2 < \text{N}_2 < \text{F}_2$ (d) $\text{F}_2 < \text{Cl}_2 < \text{O}_2 < \text{N}_2$
- Standard electrode potentials are
 Fe^{2+}/Fe ; $E^\circ = -0.44 \text{ V}$
 $\text{Fe}^{3+}/\text{Fe}^{2+}$; $E^\circ = +0.77 \text{ V}$
If Fe^{2+} , Fe^{3+} and Fe block are kept together then
(a) Fe^{3+} increases
(b) Fe^{3+} decreases
(c) $\text{Fe}^{2+}/\text{Fe}^{3+}$ remains unchanged
(d) Fe^{2+} decreases.
- Which of the following will give a pair of enantiomorphs?
(a) $[\text{Cr}(\text{NH}_3)_6] [\text{Co}(\text{CN})_6]$
(b) $[\text{Co}(\text{en})_2\text{Cl}_2] \text{Cl}$
(c) $[\text{Pt}(\text{NH}_3)_4] [\text{PtCl}_6]$
(d) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2] \text{NO}_2$
- The correct order of $\text{C}-\text{O}$ bond length among CO , CO_3^{2-} , CO_2 is
(a) $\text{CO} < \text{CO}_3^{2-} < \text{CO}_2$ (b) $\text{CO}_3^{2-} < \text{CO}_2 < \text{CO}$
(c) $\text{CO} < \text{CO}_2 < \text{CO}_3^{2-}$ (d) $\text{CO}_2 < \text{CO}_3^{2-} < \text{CO}$
- In compounds of type ECl_3 , where $\text{E} = \text{B, P, As}$ or Bi , the angles $\text{Cl}-\text{E}-\text{Cl}$ for different E are in the order
(a) $\text{B} > \text{P} = \text{As} = \text{Bi}$ (b) $\text{B} > \text{P} > \text{As} > \text{Bi}$
(c) $\text{B} < \text{P} = \text{As} = \text{Bi}$ (d) $\text{B} < \text{P} < \text{As} < \text{Bi}$
- The correct order of equivalent conductance at infinite dilution of LiCl , NaCl and KCl is
(a) $\text{LiCl} > \text{NaCl} > \text{KCl}$ (b) $\text{KCl} > \text{NaCl} > \text{LiCl}$
(c) $\text{NaCl} > \text{KCl} > \text{LiCl}$ (d) $\text{LiCl} > \text{KCl} > \text{NaCl}$
- When 1 mole of monoatomic ideal gas at $T \text{ K}$ undergoes adiabatic change under a constant external pressure of 1 atm, volume changes from 1 L to 2 L. The final temperature in kelvin would be
(a) $\frac{T}{2^{2/3}}$ (b) $T + \frac{2}{3 \times 0.0821}$
(c) T (d) $T - \frac{2}{3 \times 0.0821}$

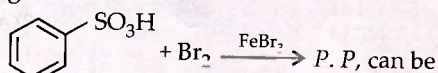
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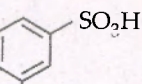
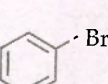
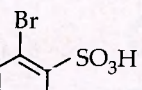
ORGANIC CHEMISTRY

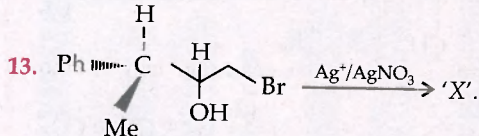


- (a)  (b) 
(c)  (d) None of these.

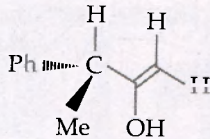
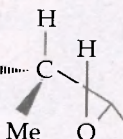
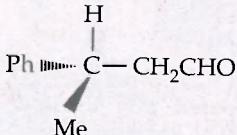
12. Which of the following options are correct for the given reaction?

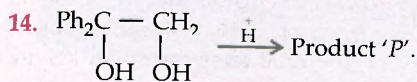


- (a)  (b) 
(c)  (d) No substitution occurs.

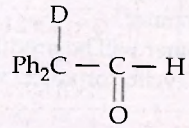
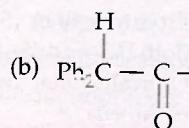


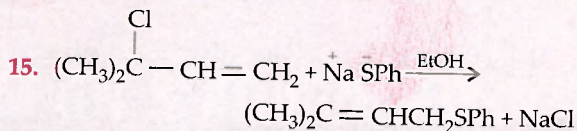
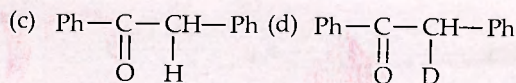
'X' should be

- (a)  (b) 
(c)  (d) None of these.



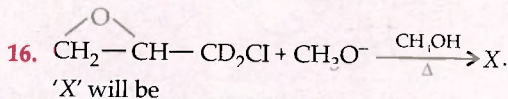
'P' will be

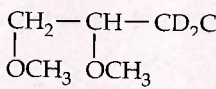
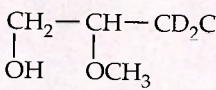
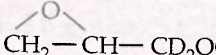
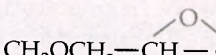
- (a)  (b) 

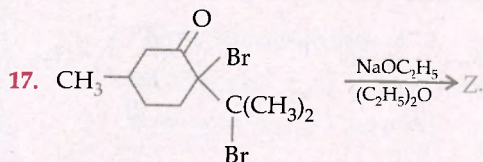


Which mechanism is followed in the above reaction?

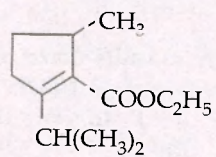
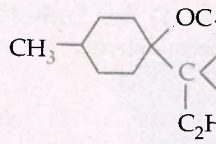
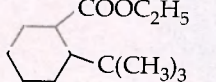
- (a) S_N2 (b) S_N1
(c) S_N2' (d) S_N1'



- (a)  (b) 
(c)  (d) 

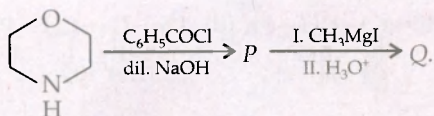


'Z' can be

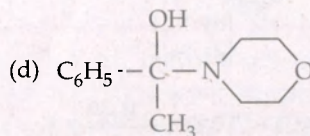
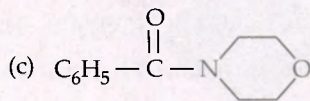
- (a)  (b) 
(c) 

(d) Reaction is not possible due to the presence of bulky group at the attacking site.

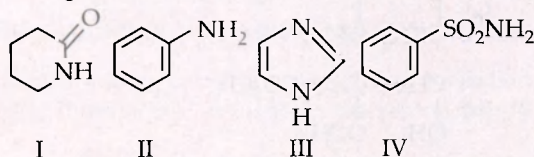
18. The major product (Q) formed in the reaction sequence is



- (a) $\text{C}_6\text{H}_5\text{COCH}_3$ (b) $\text{C}_6\text{H}_5 - \text{CO}(\text{CH}_3)_2$

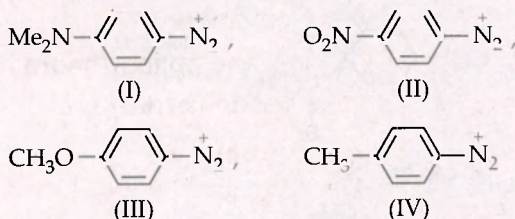


19. From the following compounds which is the strongest base and which is the strongest acid?



- (a) II : strongest base, I : strongest acid
 (b) IV : strongest base, III : strongest acid
 (c) III : strongest base, IV : strongest acid
 (d) II : strongest base, III : strongest acid.

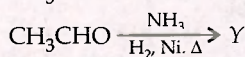
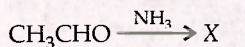
20. Consider the following diazonium ions.



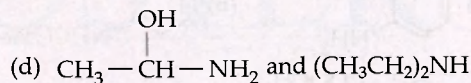
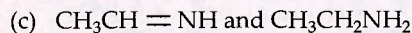
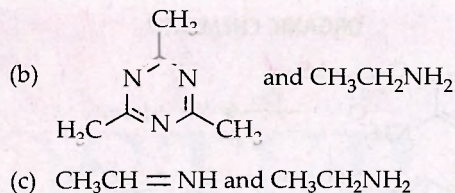
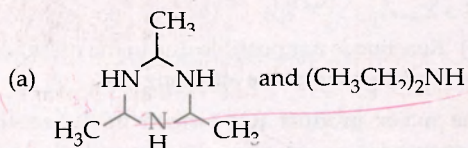
The order of reactivity towards diazo-coupling with phenol in the presence of dil. NaOH is

- (a) $\text{I} < \text{IV} < \text{II} < \text{III}$ (b) $\text{I} < \text{III} < \text{IV} < \text{II}$
 (c) $\text{III} < \text{I} < \text{II} < \text{IV}$ (d) $\text{III} < \text{I} < \text{IV} < \text{II}$

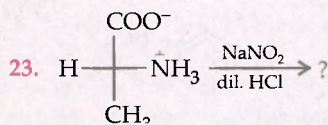
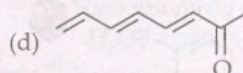
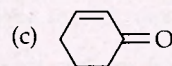
21. The products (X) and (Y) are formed in two separate reactions of acetaldehyde.



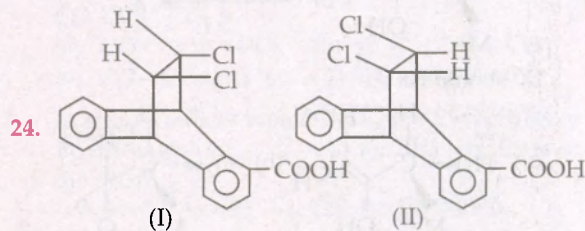
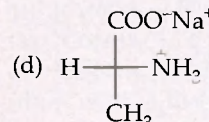
X and Y are respectively



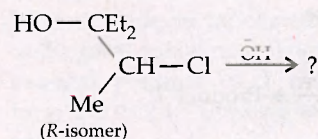
22. The compound having the highest dipole moment is



- (a) $(+)\text{CH}_3\text{CHOHCOOH}$
 (b) $(\pm)\text{CH}_3\text{CHOHCOOH}$
 (c) $(-)\text{CH}_3\text{CHOHCOOH}$



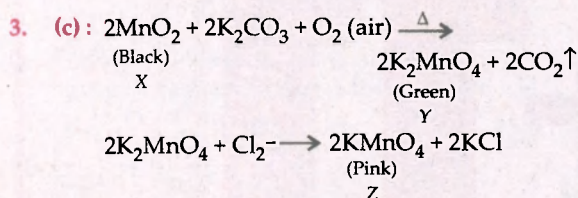
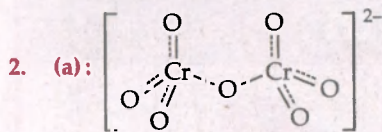
- (a) pK_a of I $>$ pK_a of II
 (b) pK_a of I $<$ pK_a of II
 (c) pK_a of I = pK_a of II
 (d) Can't be compared due to slow rate of dissociation of II.



- (a) Product will be again (R)-isomer
 (b) Product will be (S)-isomer
 (c) Both (R)- and (S)-isomer will be produced
 (d) Optically inactive cyclic product will be obtained.

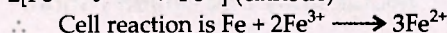
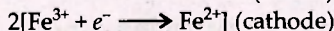
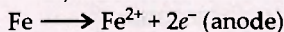
SOLUTION

1. (c): As we move along the period, the nuclear charge increases and size of atom decreases. So, the order of ionization energy is $F > N > C$. But ionization enthalpy of boron is low as compared to beryllium as first e^- of boron is to be removed from p -orbital, while in beryllium, it has to be removed from s -orbital.



4. (b): Bond length decreases as the multiplicity of bond increases.
 Therefore, $\text{N} \equiv \text{N} < \text{O} = \text{O} < \text{F} - \text{F}$
 Further, chlorine is bigger in size than fluorine, therefore bond length of $\text{F}_2 < \text{Cl}_2$.

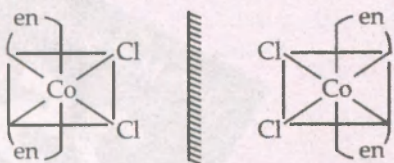
5. (b): $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$, $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = +0.77 \text{ V}$.
 If a cell is constructed combining these two electrodes, oxidation occurs at Fe^{2+}/Fe electrode.



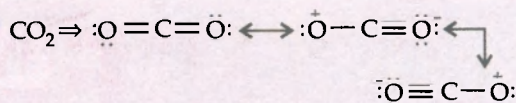
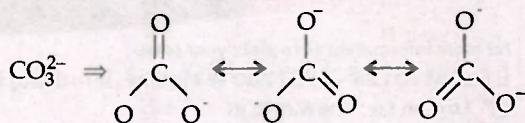
If Fe^{2+} , Fe^{3+} and Fe blocks are kept together, then Fe^{3+} reacts with Fe to yield Fe^{2+} .

$\therefore \text{Fe}^{3+}$ decreases.

6. (b): Either a pair of crystals, molecules or compounds that are mirror images of each other but are not identical and that rotate the plane of polarized light equally, but in opposite direction are called as enantiomorphs.



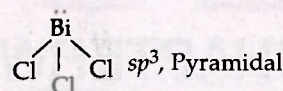
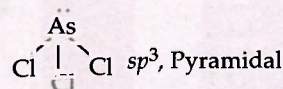
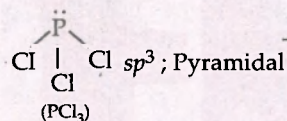
7. (c): $\text{CO} \Rightarrow \text{:}\ddot{\text{C}} \equiv \ddot{\text{O}}\text{:} \longleftrightarrow \text{:}\text{C} = \ddot{\text{O}}\text{:}$



More is the single bond character in resonance hybrid, more is the bond length.

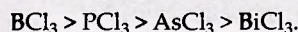
Hence, $\text{CO} < \text{CO}_2 < \text{CO}_3^{2-}$.

8. (h): sp^2 , Trigonal geometry;
Bond angle = 120°



Bond angle $< 109^\circ 28'$ and decreases from PCl_3 to BiCl_3 .

\therefore Order of bond angles is



9. (b)

10. (d): For adiabatic change, $\Delta E = W_{ad}$

$$\Delta E = nC_v (T_2 - T_1)$$

$$W_{ad} = -P(V_2 - V_1)$$

$$\therefore nC_v (T_2 - T_1) = -P(V_2 - V_1)$$

$$= -1(2 - 1)$$

$$\therefore n \cdot \frac{R}{\gamma - 1} (T_2 - T_1) = -1$$

$$\left(C_p - C_v = R, \frac{C_p}{C_v} - 1 = \frac{R}{C_v} \therefore \gamma - 1 = \frac{R}{C_v} \therefore C_v = \frac{R}{\gamma - 1} \right)$$

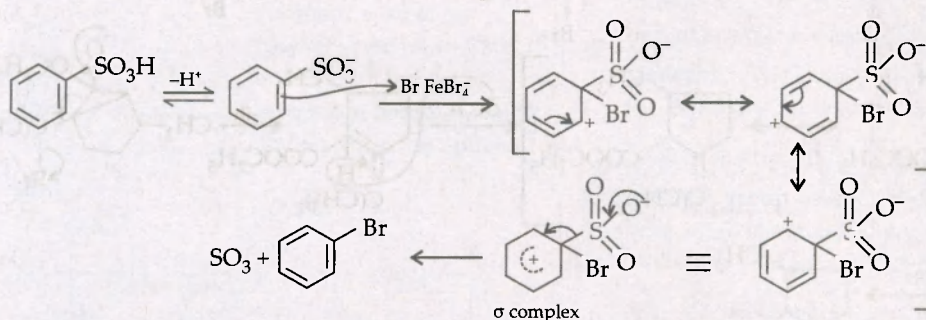
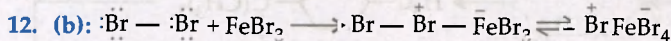
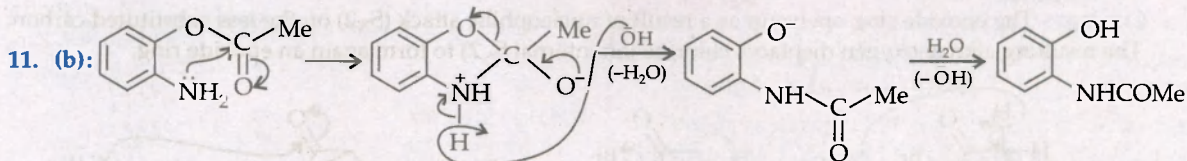
now, $n = 1$

$\gamma = 5/3$ (for monoatomic gas)

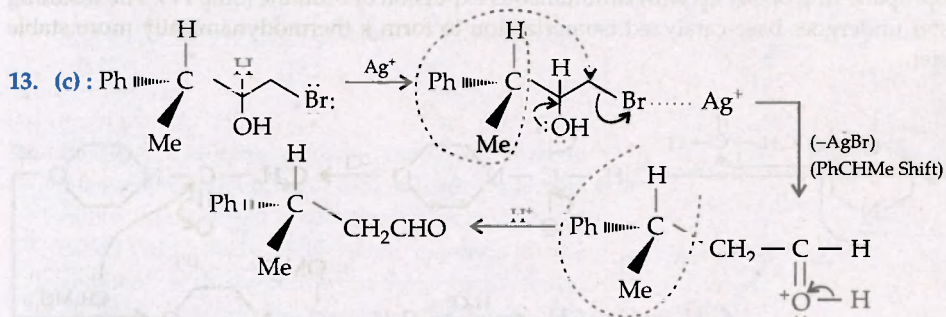
$$R = 0.0821 \text{ L-atm mol}^{-1} \text{ K}^{-1}$$

$$\therefore 1 \cdot \frac{0.0821}{\frac{5}{3} - 1} (T_2 - T_1) = -1$$

$$\Rightarrow T_2 = T_1 - \frac{2}{(3 \times 0.0821)}$$



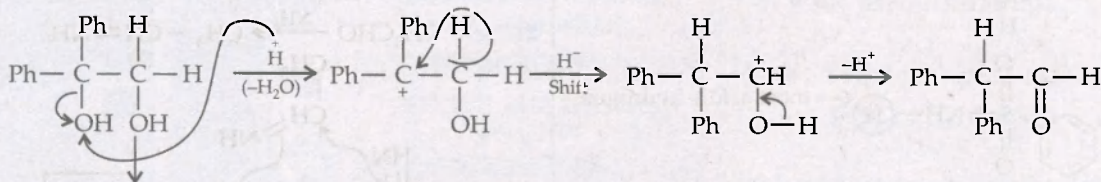
Concept : Above reaction is an example of 'ipso-substitution'. In some cases of electrophilic aromatic substitution (displacement) of one ring by another occurs. This process is 'ipso-substitution' (latin 'ipso' means 'on itself').



Concept : Bulkier PhCHMe shift takes place without hydride shift.

The configuration of the migrating chiral alkyl group is retained because it doesn't become free during rearrangement.

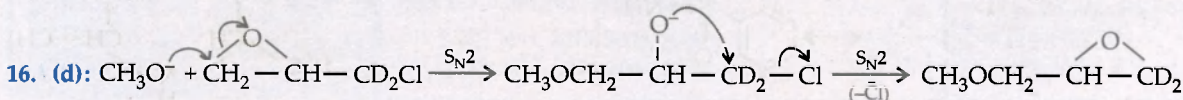
14. (b): Its a type of pinacol-pinacolone rearrangement. A close look to the reaction mechanism will give us the actual product.



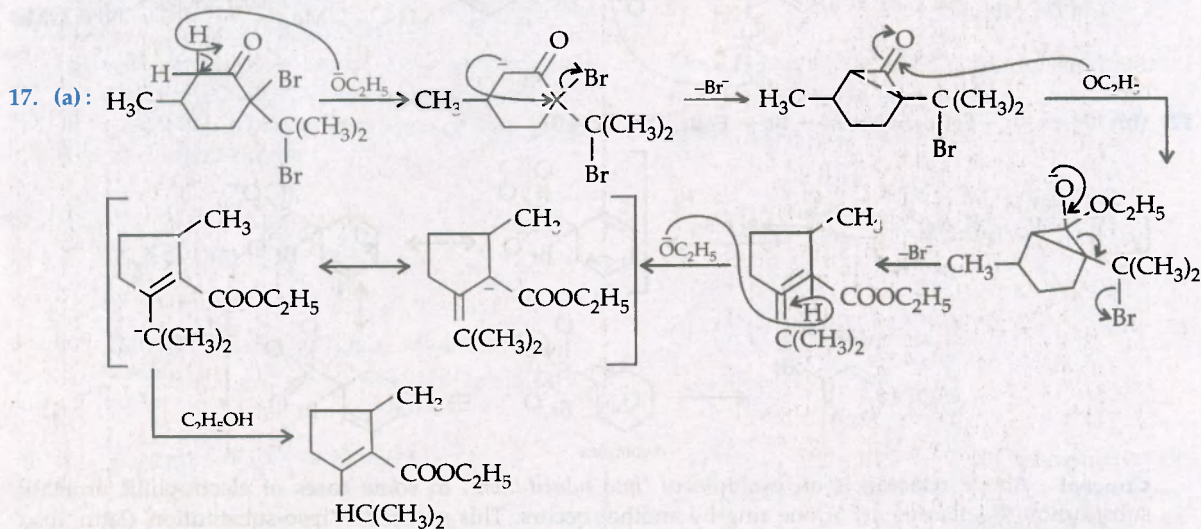
This -OH will not be attacked as it will form the less stable carbocation.

Concept : No atom of -'D' i.e., deuterium will be attacked as the reaction is purely intramolecular.

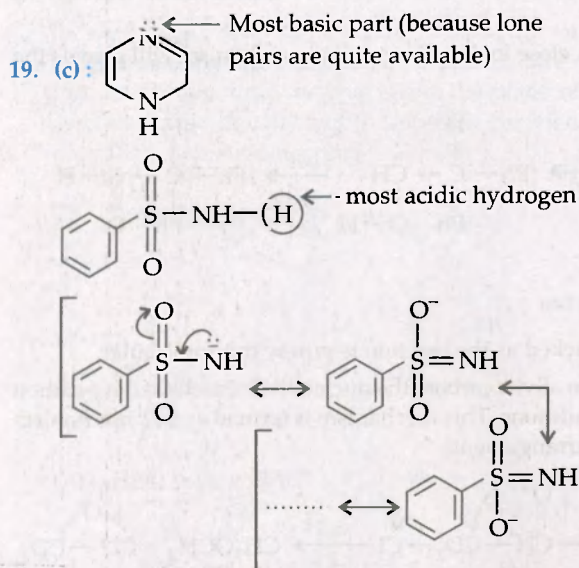
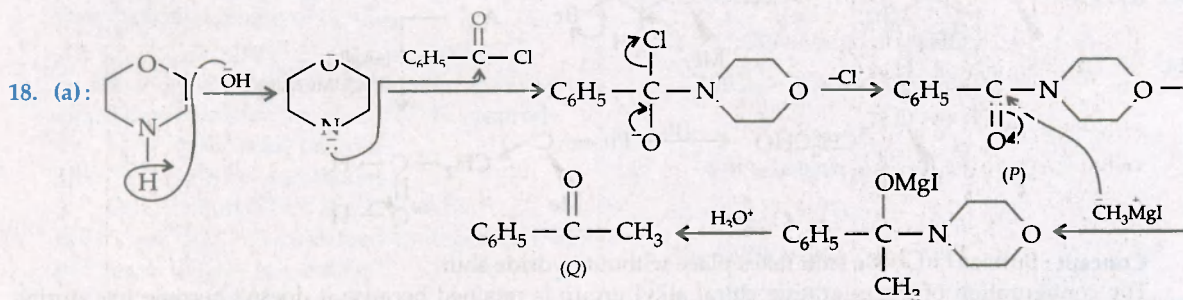
15. (c) : When steric factors prevent normal $\text{S}_{\text{N}}2$ attack at an allylic carbon, the nucleophile attacks at the γ -carbon i.e., an allylic rearrangement takes place under $\text{S}_{\text{N}}2$ conditions. This mechanism is termed as $\text{S}_{\text{N}}2'$ mechanism (bimolecular nucleophilic substitution with allylic rearrangement).



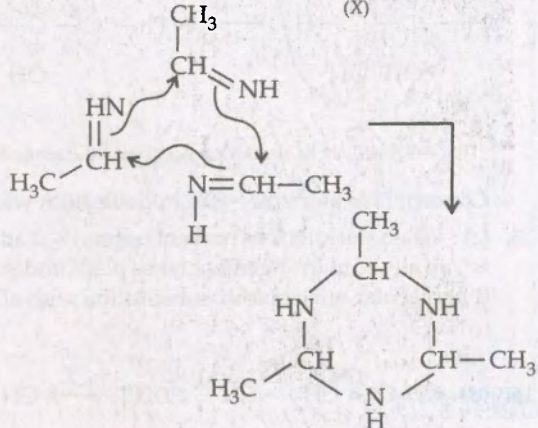
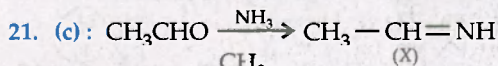
Concept : The epoxide ring opens up as a result of nucleophilic attack (S_N2) on the less substituted carbon. The resulting alkoxy oxygen displaces chlorine (an internal S_N2) to form again an epoxide ring.

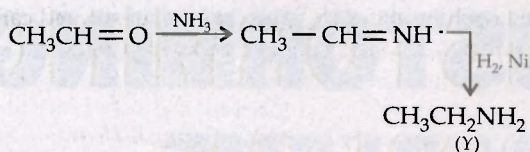


Concept : The cyclopropane ring opens up with simultaneous expulsion of bromine (Step IV). The resulting β , γ -unsaturated ester undergoes base-catalyzed isomerization to form a thermodynamically more stable α , β -unsaturated ester.

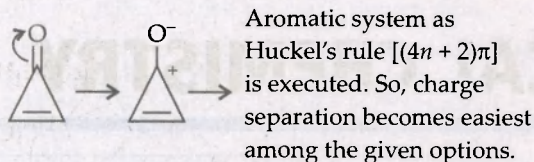


20. (b): Diazonium ion acts as an electrophile in coupling reaction; greater the electron withdrawing power, higher the electrophilicity.

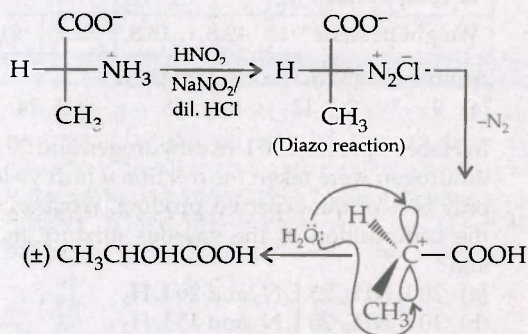




22. (b):



23. (b):

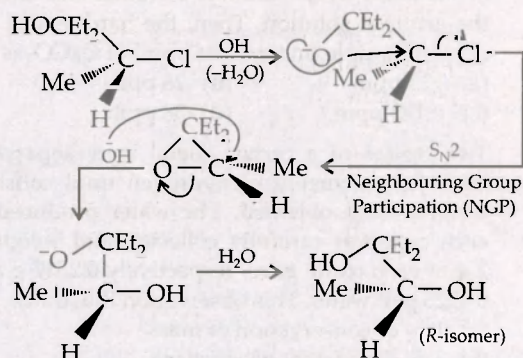


24. (a): The inductive effects may be directly transmitted through space or solvent molecules rather than along a chain. Such effects are often called field effects. Field effects depends on the geometry of the molecule but the inductive effect depends only on the nature of the bonds. For example, in the isomeric dichloroacids I and II,

the inductive effect of the chlorine atoms on the position of electrons in the $-\text{COOH}$ group and therefore on acidity should be same since the same bonds intervene, but the field effect disfavours the dissociation of I but favours the dissociation of II because the $-\text{Cl}$ atoms are closer in space to the $-\text{COOH}$ group in I than they are in II and because of this I is less acidic than II.

Concept : The conjugate base I is destabilized by repulsive interaction because the negative ends of the two $\delta^+ - \delta^-$ $\text{C} - \text{Cl}$ dipoles are closer to the $-\text{COO}^-$ group on the other hand the conjugate base of II is stabilized by electrostatic force of attraction because the positive ends of the two $\delta^+ - \delta^-$ $\text{C} - \text{Cl}$ dipoles are closer to the $-\text{COO}^-$ group.

25. (a):



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BRAINSTORMING PROBLEMS

PHYSICAL CHEMISTRY

SOME BASIC CONCEPTS OF CHEMISTRY

1. A 500 mL sample of the effluent from a water softener required 6 drops of standard soap solution to produce a permanent lather. The soap solution had been calibrated against an artificial hard water solution containing 0.136 g of CaCl_2 per litre. On the average, it required 28 drops of standard soap solution to lather 500 mL of the artificial solution. Then, the hardness of the effluent sample (in terms of ppm) of CaCO_3 is
(a) 123 ppm (b) 26 ppm
(c) 0.123 ppm (d) 38 ppm
2. Two oxides of a certain metal were separately heated in a current of hydrogen until constant weights were obtained. The water produced in each case was carefully collected and weighed. 2 g of each oxide gave, respectively 0.2517 g and 0.4526 g of water. This observation illustrates
(a) law of conservation of mass
(b) law of constant proportions
(c) law of multiple proportions
(d) law of reciprocal proportions
3. H_3PO_4 is a tribasic acid and one of its salts is NaH_2PO_4 . What volume of 1 M NaOH should be added to 12 g NaH_2PO_4 (mol. wt. 120) to exactly convert it into Na_3PO_4 ?
(a) 100 mL (b) 300 mL (c) 200 mL (d) 80 mL
4. An element 'M' combines with oxygen, hydrogen, chlorine and fluorine to form respective compounds containing 56.36, 91.17, 22.54 and 35.22 percent of 'M', respectively. The vapour densities of these compounds (H = 1) are 110, 17, 68.75 and 44 respectively. Atomic weight of the element 'M' is
(a) 39 (b) 31 (c) 92 (d) 23
5. An element 'L' forms various compounds, their weight percent of 'L' has been indicated below:

Compounds of 'L'	I	II	III	IV
------------------	---	----	-----	----

Vapour density of compounds	14	38	14	22
Weight percent	42.8	15.8	85.7	81.4

Atomic weight of the element 'L' is

- (a) 9 (b) 12 (c) 15 (d) 24
6. In Haber's process, 30 L of dihydrogen and 30 L of dinitrogen were taken for reaction which yielded only 50% of the expected product. What will be the composition of the gaseous mixture in the end?
(a) 20 L NH_3 , 25 L N_2 and 20 L H_2
(b) 10 L NH_3 , 25 L N_2 and 15 L H_2
(c) 20 L NH_3 , 10 L N_2 and 30 L H_2
(d) 20 L NH_3 , 25 L N_2 and 15 L H_2

STRUCTURE OF ATOM

7. In Bohr series of lines of hydrogen spectrum, the third line from the red end corresponds to which one of the following inter-orbit jumps of the electron for Bohr orbit in an atom of hydrogen?
(a) $5 \rightarrow 2$ (b) $4 \rightarrow 1$ (c) $2 \rightarrow 5$ (d) $13 \rightarrow 2$
8. The value of Planck's constant is 6.63×10^{-34} J s. The velocity of light is 3.0×10^8 m s^{-1} . Which value is closest to the wavelength (in nm) of a quantum of light with frequency of 8×10^{15} s^{-1} ?
(a) 2×10^{-25} (b) 5×10^{-18}
(c) 4×10 (d) 3×10^7
9. The uncertainty in the velocity of a cricket ball of mass 100 g, when uncertainty in its position is of the order of 1 \AA , would be
(a) $> 5.27 \times 10^{-24}$ m s^{-1} (b) $> 2.35 \times 10^{-23}$ m s^{-1}
(c) $> 3.16 \times 10^{-22}$ m s^{-1} (d) $> 8.51 \times 10^{-24}$ m s^{-1}
10. When a certain metal was irradiated with a light of frequency 3.2×10^{16} Hz, the photoelectrons emitted had twice the kinetic energy as did photoelectrons emitted when the same metal was irradiated with light frequency 2.0×10^{16} Hz. Hence, threshold frequency is
(a) 8×10^{17} Hz (b) 0.8×10^{15} Hz
(c) 8×10^{15} Hz (d) 8×10^{16} Hz

11. Light of wavelength λ shines on a metal surface with intensity x and the metal emits y electrons per second of average energy, z . What will happen to y and z if x is doubled?

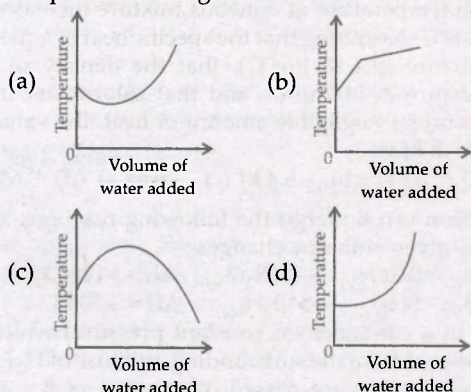
- y will be doubled and z will become half.
- y will remain same and z will be doubled.
- both y and z will be doubled.
- y will be doubled but z will remain same.

12. The nucleus of an atom can be assumed to be spherical. The radius of the nucleus of mass number A is given by $1.25 \times 10^{-13} \times A^{1/3}$ cm. Radius of atom is 1 Å. If the mass number is 64, then the fraction of the atomic volume that is occupied by the nucleus is

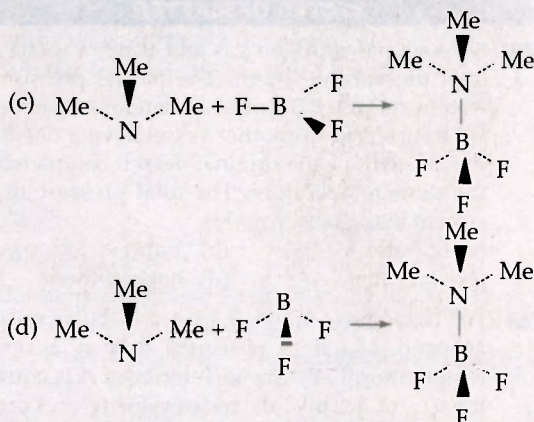
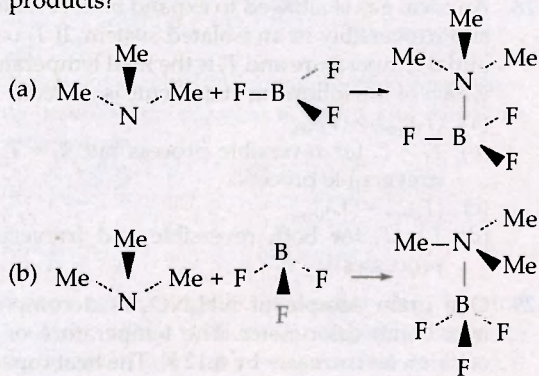
- 1.0×10^{-3}
- 5.0×10^{-5}
- 2.5×10^{-2}
- 1.25×10^{-13}

CHEMICAL BONDING AND MOLECULAR STRUCTURE

13. When water is stirred with glucose, strong hydrogen bonds are initially formed between glucose molecules and water molecules, but as more water is added, these hydrogen bonds are broken. Which graph represents the observed temperature changes?



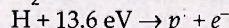
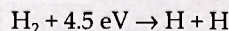
14. Trimethylamine Me_3N , reacts with boron trifluoride, BF_3 , to form a compound of formula $\text{Me}_3\text{N} \cdot \text{BF}_3$. How may this reaction be written in terms of the shapes of the reactants and products?



15. Which set of properties could apply to a non-ionic compound which has a giant lattice?

Physical state at room temp.	Electrical conductivity of the molten compound	Melting point (°C)
(a) Liquid	does not conduct	-114
(b) Liquid	does not conduct	melts over a temperature range
(c) Solid	conduct well	808
(d) Solid	does not conduct	1610

16. What conclusions can be drawn from the following reactions?



- It is more difficult to break up an H_2 molecule than to break up a hydrogen atom.
- It is easier to break up an H_2 molecule than to break up a hydrogen atom.
- The average energy of formation of H and p^+ are the same.
- None of these.

17. The radius and charge of each of six ions are shown in the table

Ion	J^+	L^+	M^{2+}	X^-	Y^-	Z^{2-}
Radius/nm	0.14	0.18	0.15	0.14	0.18	0.15

The ionic solids JX , LY and MZ are of the same lattice type. What is the correct order of their lattice energies placing the one with the highest numerical value first?

- $\text{JX} > \text{LY} > \text{MZ}$
- $\text{JX} > \text{MZ} > \text{LY}$
- $\text{LY} > \text{MZ} > \text{JX}$
- $\text{MZ} > \text{JX} > \text{LY}$

18. What fraction of charge is present on I in covalently bonded $\text{H}-\text{I}$, if the dipole moment of HI is 0.38 C and the bond length is 1.61 Å?

- 5%
- 16%
- 33%
- 79%

STATES OF MATTER

19. A vessel has nitrogen gas and water vapour at a total pressure of 1 atm. The partial pressure of water vapour is 0.3 atm. The contents of this vessel are transferred to another vessel having one third the capacity of the original vessel, completely at the same temperature. The total pressure of the system in the new vessel is
 (a) 2.7 atm (b) 1 atm
 (c) 3.33 atm (d) none of these.
20. For two gases, A and B with molecular weights M_A and M_B , it is observed that at a certain temperature T , the mean velocity of A is equal to the u_{rms} of B. Thus, the mean velocity of A can be made equal to the mean velocity of B, if
 (a) A is at temperature T and B at T' ; $T > T'$
 (b) both A and B are raised to a higher temperature
 (c) both A and B are lowered in temperature
 (d) none of these.
21. A mixture of 50.0 mL of NH_3 and 60.0 mL of O_2 gas reacts as

$$4\text{NH}_{3(g)} + 5\text{O}_{2(g)} \rightarrow 4\text{NO}_{(g)} + 6\text{H}_2\text{O}_{(g)}$$
 If all the gases are at the same temperature and pressure, and the reaction continues until one of the gases is completely consumed, what volume of water vapour is produced?
 (a) 48 mL (b) 60.0 mL
 (c) 72 mL (d) 75.0 mL
22. A flask contains 12 g of a gas of molecular mass 120 at a pressure of 100 atm was evacuated by means of a pump until the pressure was 0.01 atm. Which of the following is the best estimate of the number of molecules left in the flask ($N = 6 \times 10^{23} \text{ mol}^{-1}$)?
 (a) 6×10^{19} (b) 6×10^{18}
 (c) 6×10^{17} (d) 6×10^{13}
23. Gaseous benzene reacts with hydrogen gas in presence of a nickel catalyst to form gaseous cyclohexane according to the reaction:

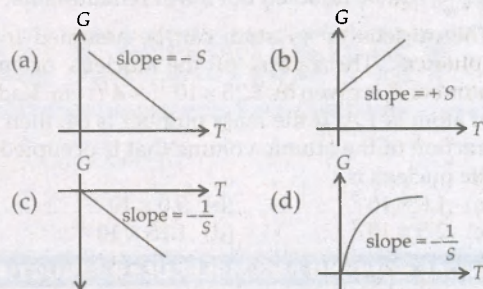
$$\text{C}_6\text{H}_{6(g)} + 3\text{H}_{2(g)} \rightarrow \text{C}_6\text{H}_{12(g)}$$
 A mixture of C_6H_6 and excess H_2 has a pressure of 60 mm of Hg in an unknown volume. After the gas had been passed over a nickel catalyst and all the benzene converted to cyclohexane, the pressure of the gas was 30 mm of Hg in the same volume at the same temperature. The fraction of C_6H_6 (by volume) present in the original volume is
 (a) 1/3 (b) 1/4 (c) 1/5 (d) 1/6
24. Two glass bulbs A and B are connected by a very small tube having a stop-cock. Bulb A has a volume of 100 cm^3 and contained the gas while bulb B was empty. On opening the stop-cock, the

pressure fell down to 40%. The volume of the bulb B must be

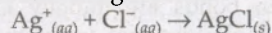
- (a) 75 cm^3 (b) 125 cm^3
 (c) 150 cm^3 (d) 250 cm^3

THERMODYNAMICS

25. For a pure substance, a plot of Gibb's free energy (G) against temperature at constant pressure is



26. Consider the following reaction:



When 10.0 mL of 1.00 M AgNO_3 solution is added to 10 mL of 1.00 N NaCl solution at 25°C in a calorimeter, a white ppt. of AgCl is formed and the temperature of aqueous mixture increases to 32.6°C . Assuming that the specific heat of aqueous mixture is $4.18 \text{ J}/(\text{g}^\circ\text{C})$, that the density of the mixture is 1.00 g/mL and that calorimeter itself absorbs a negligible amount of heat, the value of ΔH in kJ is

- (a) -64 kJ (b) -6.4 kJ (c) -0.64 kJ (d) 0.64 kJ
27. Boron can undergo the following reactions with the given enthalpy changes:

$$2\text{B}_{(s)} + 3/2\text{O}_{2(g)} \rightarrow \text{B}_2\text{O}_{3(s)}; \Delta H = -1260 \text{ kJ}$$

$$2\text{B}_{(s)} + 3\text{H}_{2(g)} \rightarrow \text{B}_2\text{H}_{6(g)}; \Delta H = -30 \text{ kJ}$$
 If in a container (at constant pressure) which is isolated from the surrounding, mixture of H_2 (gas) and O_2 (gas) are passed over excess of $\text{B}_{(s)}$, then what molar ratio of oxygen and hydrogen will be used so that the temperature of the container do not change?
 (a) 1 : 42 (b) 1 : 84 (c) 42 : 1 (d) 15 : 3
28. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and T_f is the final temperature, which of the following statements is correct?
 (a) $(T_f)_{\text{irrev}} > (T_f)_{\text{rev}}$
 (b) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process.
 (c) $(T_f)_{\text{rev}} = (T_f)_{\text{irrev}}$
 (d) $T_f = T_i$ for both reversible and irreversible processes.

29. One gram sample of NH_4NO_3 is decomposed in a bomb calorimeter. The temperature of the calorimeter increases by 6.12 K . The heat capacity

of the system is 1.23 kJ/g/deg. What is the molar heat of decomposition for NH_4NO_3 ?

- (a) -7.53 kJ/mol (b) -398.1 kJ/mol
(c) -16.1 kJ/mol (d) -602 kJ/mol

30. In an oven, using 10 kg coal (assume the coal is 80% carbon in weight), insufficient oxygen is supplied such that 60% of carbon is converted to CO_2 and 40% carbon is converted to CO . The heat generated, when coal is burnt in this fashion would be :

Given, $\text{C}_{(s)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} \quad \Delta H = -394 \text{ kJ}$

$\text{C}_{(s)} + \frac{1}{2} \text{O}_{2(g)} \rightarrow \text{CO}_{(g)} \quad \Delta H = -111 \text{ kJ}$

- (a) 183200 kJ (b) 187200 kJ
(c) 185200 kJ (d) 181200 kJ

EQUILIBRIUM

31. A solution contains 0.05 M each of NaCl and Na_2CrO_4 . In both, solid AgNO_3 is gradually added. Mark out the correct statement.

(Given $K_{sp}(\text{AgCl}) = 1.7 \times 10^{-10} \text{ M}^2$ and

$K_{sp}(\text{Ag}_2\text{CrO}_4) = 1.9 \times 10^{-12} \text{ M}^3$)

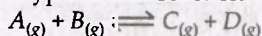
- (a) CrO_4^{2-} ions are precipitated first.
(b) Cl^- ions are precipitated first.
(c) Both Cl^- and CrO_4^{2-} ions are precipitated together.
(d) The second ion starts precipitating when half of the first ion is precipitated.

32. For a general reaction

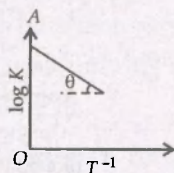
$P_{(g)} + Q_{(g)} \rightleftharpoons R_{(g)} + S_{(g)}$, the specific rate constant is $k_{\text{(forward)}} = 2.0 \times 10^{-3} \text{ mol}^{-1} \text{ L s}^{-1}$ at a certain temperature. Reaction starts with equimolar amounts of P and Q . Reaching at equilibrium, it is observed that P is twice that of R . The specific rate constant for the backward reaction is

- (a) $1.5 \times 10^2 \text{ mol}^{-1} \text{ L s}^{-1}$ (b) $5.0 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$
(c) $8.0 \times 10^{-3} \text{ mol}^{-1} \text{ L s}^{-1}$ (d) none of the above.

33. For a hypothetical reaction



a graph between $\log K$ and T^{-1} is straight line as follows, where $\theta = \tan^{-1} 0.5$ and $OA = 10$.



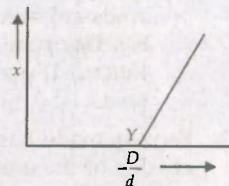
Assuming ΔH° is independent of temperature, the equilibrium constant at 298 K and 798 K are respectively,

- (a) $K_1 = 9.96 \times 10^9$, $K_2 = 2.76 \times 10^{10}$
(b) $K_1 = 3.79 \times 10^8$, $K_2 = 9.98 \times 10^9$
(c) $K_1 = 7.96 \times 10^9$, $K_2 = 7.96 \times 10^9$
(d) $K_1 = 9.98 \times 10^9$, $K_2 = 9.96 \times 10^9$
34. Before equilibrium is set-up for the chemical reaction, $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, vapour density of the gaseous mixture was measured. If D is the

theoretical value of vapour density, variation of x with D/d is shown by the graph.

What is value of D/d at point Y?

- (a) 0
(b) 1.5
(c) 1
(d) 0.5



35. Solution of aniline hydrochloride is X due to hydrolysis of Y. X and Y are

- (a) basic, $\text{C}_6\text{H}_5\text{NH}_3^+$ (b) acidic, $\text{C}_6\text{H}_5\text{NH}_3^+$
(c) basic, Cl^- (d) acidic, Cl^- .

36. If K_{sp} of $\text{Mg}(\text{OH})_2$ is 1.2×10^{-11} . Then the highest pH of the 0.1 M solution of Mg^{2+} ion from which $\text{Mg}(\text{OH})_2$ is not precipitated is

- (a) 4.96 (b) 6.96 (c) 7.54 (d) 9.04

SOLID STATE

37. In a cubic lattice each edge of the unit cell is 400 pm. Atomic weight of the element is 60 and its density is 6.25 g/c.c. Avogadro number = 6×10^{23} . The crystal lattice is

- (a) face-centred (b) primitive
(c) body-centred (d) end-centred.

38. In a cubic packed structure of mixed oxides, the lattice is made up of oxide ions, one fifth of tetrahedral voids are occupied by divalent (X^{2+}) ions. While one half of the octahedral voids are occupied by trivalent ions (Y^{3+}), then the formula of the oxide is

- (a) XY_2O_4 (b) X_2YO_4
(c) $\text{X}_4\text{Y}_5\text{O}_{10}$ (d) $\text{X}_5\text{Y}_4\text{O}_{10}$

39. ZnS exists in two crystalline structures:

- (i) Zinc blende and (ii) Wurtzite

Mark the correct statement about their structure.

- (a) In zinc blende S^{2-} ions are arranged in ccp while Zn^{2+} occupy half of the tetrahedral sites.
(b) In zinc blende S^{2-} ions are arranged in hcp and Zn^{2+} ions occupy all octahedral voids.
(c) In Wurtzite structure S^{2-} ions are arranged in ccp and Zn^{2+} ions occupy half of tetrahedral voids.
(d) In Wurtzite structures S^{2-} ions are in hcp arrangement and Zn^{2+} ions are occupying all octahedral voids.

40. Select the incorrect statements.

- (a) In closest packing of x -atoms, there are $3x$ tetrahedral holes, and x -octahedral holes.
(b) The co-ordination no. of U : O in UO_2 is 8 : 4.
(c) In hexagonal packing of oxide ion sapphire (the aluminium oxide) Al^{3+} ions crystallize in

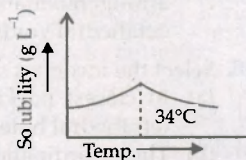
$2/3^{\text{rd}}$ of the octahedral hole, then the formula of sapphire is Al_2O_3 .

- (d) If anion constitutes ccp and all the octahedral voids are occupied by cation (A), the crystal has the same molecular formula AB, if the cation (A) occupies the alternate tetrahedral voids.

41. Ferrous oxide has a cubic structure. The length of edge of the unit cell is 5 Å. The density of the oxide is 4.0 g cm^{-3} . Then the number of Fe^{2+} and O^{2-} ions present in each unit cell will be
 (a) Four Fe^{2+} and four O^{2-}
 (b) Two Fe^{2+} and two O^{2-}
 (c) Four Fe^{2+} and two O^{2-}
 (d) Two Fe^{2+} and four O^{2-}
42. A solid AB has NaCl type structure. If the radius of cation A^+ is 170 pm, calculate the maximum possible radius of the anion B^- .
 (a) 210.3 pm (b) 397.4 pm
 (c) 410.6 pm (d) 347.9 pm

SOLUTIONS

43. Phenol associates in benzene to a certain extent to form dimer. A solution containing $2.0 \times 10^{-2} \text{ kg}$ of phenol in 1.0 kg of benzene has its freezing point decreased by 0.69 K. The degree of association of phenol is (K_f for benzene = $5.12 \text{ K kg mol}^{-1}$)
 (a) 73.4% (b) 50.1% (c) 42.3% (d) 25.1%
44. When 0.6 g of an organic acid dissolved in 200 mL of water is extracted with 50 mL of ether, it is found on analysis, that 0.4 g of the organic acid goes into the ether layer. Which of the following represents the correct ratio of the solubility of the acid in ether and water?
 (a) $\frac{S_{\text{ether}}}{S_{\text{water}}} = 0.125$ (b) $\frac{S_{\text{ether}}}{S_{\text{water}}} = 0.5$
 (c) $\frac{S_{\text{ether}}}{S_{\text{water}}} = 2$ (d) $\frac{S_{\text{ether}}}{S_{\text{water}}} = 8$
45. The degree of dissociation (α) of a weak electrolyte A_xB_y is related to van't Hoff factor (i) by the expression
 (a) $\alpha = \frac{i-1}{(x+y-1)}$ (b) $\alpha = \frac{i-1}{x+y+1}$
 (c) $\alpha = \frac{x+y-1}{i-1}$ (d) $\alpha = \frac{x+y+1}{i-1}$
46. Solubility curve of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in water with temperature is given as shown in the figure. From the figure, we can say that
 (a) solution process is exothermic

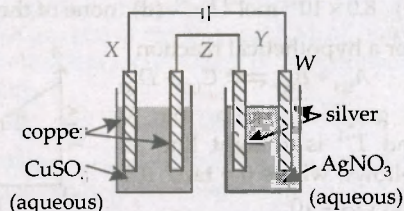


- (b) solution process is exothermic till 34°C and endothermic after 34°C
 (c) solution process is endothermic till 34°C and exothermic thereafter
 (d) solution process is endothermic.

47. 0.100 g of non-volatile solute is added to 1 L of each acetic acid, benzene, naphthalene and water. Which of the following is correct decreasing order of freezing point of the corresponding solutions?
 (a) Naphthalene > benzene > acetic acid > water
 (b) Water > acetic acid > benzene > naphthalene
 (c) Naphthalene > acetic acid > benzene > water
 (d) Water > benzene > acetic acid > naphthalene.
48. A current of dry air was bubbled through a bulb containing 26.66 g of an organic substance in 200 g of water, then through a bulb at the same temperature containing pure water and finally through a tube containing fused CaCl_2 . The loss of weight of water bulb = 0.0870 g and the gain of the weight of CaCl_2 tube = 2.036 g. The molecular weight of the organic substance is
 (a) 56 (b) 41 (c) 78 (d) 67

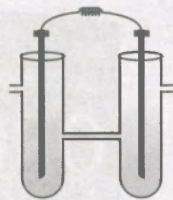
ELECTROCHEMISTRY

49. Concentration polarization arises because of the
 (a) different concentrations of solutions in the two half-cells
 (b) changes in the concentration of electrolyte around the electrode from bulk concentration
 (c) reversible nature of the cell
 (d) variation in temperature during measurements.
50. During electrolysis in the cell shown, 1.05 g copper is deposited on electrode X. Which one of the following statements is correct? (Relative atomic masses $\text{Cu} = 63$, $\text{Ag} = 108$).
 (a) The mass of silver electrode W increases by 3.60 g.
 (b) The mass of silver deposited on electrode Y during the electrolysis is 1.80 g.
 (c) Z is a salt-bridge.
 (d) The concentration of copper ions in solution decreases during electrolysis.
51. Equivalent conductance of 1 M propanoic acid is $10 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$ and that at infinite dilution $200 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$. pH of the acid solution is
 (a) 7 (b) 3.3 (c) 1.3 (d) 6.8



52. The molar ionic conductivities of NH_4^+ and OH^- at infinite dilution are 72 and $198 \text{ ohm}^{-1} \text{ cm}^2$ respectively. The molar conductivity of a centinormal NH_4OH solution at the same temperature is found to be $9 \text{ ohm}^{-1} \text{ cm}^2$. The percentage dissociation of NH_4OH at this concentration will be
(a) 3.33% (b) 7.14% (c) 12.5% (d) 4.54%

53. Two weak acid solutions HA_1 and HA_2 each with the same concentration and having $\text{p}K_a$ values 3 and 5 are placed in contact with hydrogen electrode (1 atm, 25°C) and are interconnected through a salt bridge. The emf of the cell is



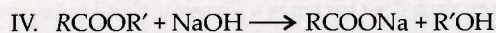
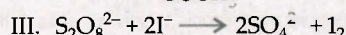
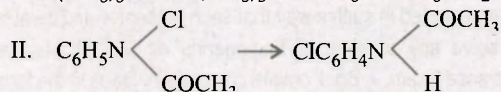
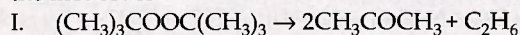
- (a) 0.21 V (b) 0.059 V (c) 0.018 V (d) 0.021 V

54. κ_1 and κ_2 are specific conductance of the solutions A and B in the same conductivity cell. If equal volumes of solutions A and B are mixed, what will be the resistance of the mixture using the same conductivity cell, whose cell constant is x ? (Assume there is no change in the degree of dissociation on mixing)

- (a) $R = \frac{\kappa_1 + \kappa_2}{2x}$ (b) $R = \frac{2(\kappa_1 + \kappa_2)}{x}$
(c) $R = 2x(\kappa_1 + \kappa_2)$ (d) $R = \frac{2x}{\kappa_1 + \kappa_2}$

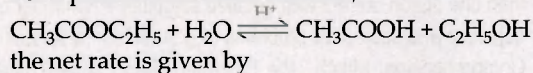
CHEMICAL KINETICS

55. Which of the following given reaction(s) is/are of the first order?



- (a) Only I and IV (b) Only I and II
(c) Only I and III (d) All of these.

56. For a pseudo first order reaction,



$$\frac{dx}{dt} = 4 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1} [(\text{CH}_3\text{COOC}_2\text{H}_5)] - 3 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1} [\text{CH}_3\text{COOH}][\text{CH}_2\text{H}_5\text{OH}]$$

Then, the equilibrium constant of the reaction of the reaction would be

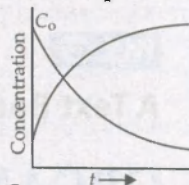
- (a) $1.3 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$
(b) $1.3 \times 10^{-1} \text{ mol L}^{-1} \text{ s}^{-1}$
(c) $1.33 \times 10^{-9} \text{ mol L}^{-1}$
(d) $1.33 \times 10^{-8} \text{ mol L}^{-1}$

57. Consider following reactant sample

- I. 1 mol of A and 1 mol of B in a 1 L vessel
II. 2 mol of A and 2 mol of B in a 2 L vessel
III. 0.2 mol of A and 0.2 mol of B in a 0.1 L vessel
Which of the reactant sample reacts at the highest rate?

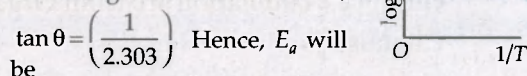
- (a) I (b) II
(c) III (d) All are at equal rate.

58. The concentration of B at the point of intersection of the two curves as shown in the figure for, $A \rightarrow nB$, is



- (a) $\frac{nC_0}{2}$ (b) $\frac{nC_0}{n-1}$
(c) $\frac{nC_0}{n+1}$ (d) $\left(\frac{n-1}{n+1}\right)C_0$

59. Graph between $\log k$ and $\frac{1}{T}$ is a straight line with $\text{OX} = 5$,



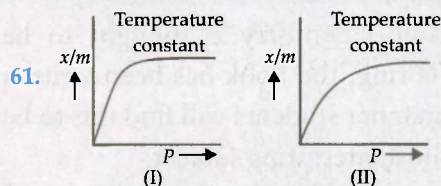
$\tan \theta = \left(\frac{1}{2.303}\right)$ Hence, E_a will be

- (a) $2.303 \times 2 \text{ cal}$ (b) $\frac{5}{2.303} \text{ cal}$
(c) -2 cal (d) none of these.

60. The reaction $A \rightarrow B$ follows first order kinetics. The time taken for 0.8 mole of A to produce 0.6 mole of B is 1 hr. What is the time taken for conversion of 0.9 mole of A to produce 0.675 mole of B?

- (a) 1 hr (b) 0.5 hr (c) 0.25 hr (d) 2 hr

SURFACE CHEMISTRY



61.

Which is the correct statement?

- (a) (I) represents Freundlich's adsorption isotherm while (II) represents Langmuir's adsorption isotherm.
(b) (I) represents Langmuir's adsorption isotherm while (II) represents Freundlich's adsorption isotherm.
(c) Both Freundlich and Langmuir adsorption isotherms have been found to be applicable in the adsorption of gases on solids only.
(d) Change of pressure affects a lot and further adsorption can take place in both the isotherms.

62. Potassium stearate is obtained by the saponification of an oil or a fat. It has formula $\text{CH}_3 - (\text{CH}_2)_{16} - \text{COO}^- \text{K}^+$. The molecule has a lyophobic end ($\text{CH}_3 -$) and a lyophilic end $\text{COO}^- \text{K}^+$. Potassium stearate is an example for
 (a) lyophobic colloid
 (b) lyophilic colloid
 (c) multimolecular colloid
 (d) associated colloid or micelle.

63. The equation for Langmuir adsorption isotherm under high pressure is

$$\begin{array}{ll} \text{(a)} \quad \frac{x}{m} = \frac{a}{b} & \text{(b)} \quad \frac{x}{m} = aP \\ \text{(c)} \quad \frac{x}{m} = \frac{1}{aP} & \text{(d)} \quad \frac{x}{m} = \frac{b}{a} \end{array}$$

64. The gold numbers of P , Q , R and S are 0.04, 0.002, 10 and 25 respectively. The protective powers of P , Q , R and S are in the order

- (a) $P > Q > R > S$ (b) $Q > P > R > S$
 (c) $S > R > Q > P$ (d) $R > P > Q > S$

NUCLEAR CHEMISTRY

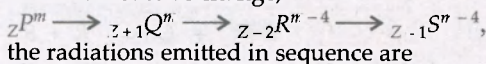
65. The counting rate observed from radioactive source at $t = 0$ second was 1600 counts/s and at $t = 8$ s it was 100 counts/s. The counting rate observed as count per s at $t = 6$ s will be

- (a) 400 (b) 300 (c) 200 (d) 150

66. The mass of helium atom of mass number 4 is 4.0026 amu, while that of the neutron and proton are 1.0087 and 1.0078 respectively on the same scale. Hence the nuclear binding energy per nucleon in the helium atom is nearly

- (a) 5 MeV (b) 7 MeV
 (c) 10 MeV (d) 14 MeV

67. In the radioactive change,



- (a) α, β, γ (b) β, α, γ
 (c) γ, α, β (d) β, γ, α

68. 1 g atom of an α -emitting nuclide ${}_Z^A X$ ($t_{1/2} = 10$ hr) was placed in a sealed container. 4.52×10^{23} He atoms will accumulate in the container in

- (a) 4.52 hr (b) 9.40 hr (c) 10.0 hr (d) 20.0 hr

69. The radio nuclide ${}_{90}^{234}\text{Th}$ undergoes two successive β -decays followed by one α -decay. The atomic number and the mass number respectively of the resulting radionuclide are

- (a) 94 and 230 (b) 90 and 230
 (c) 92 and 230 (d) 92 and 234

70. The $t_{1/2}$ of radioactive K-40 is 5.27 years ($\lambda = 2.5 \times 10^{-7} \text{ min}^{-1}$). The decay activity of 2.0 g of the sample is about

- (a) $7.5 \times 10^{15} \text{ dpm}$ (b) $5 \times 10^5 \text{ dpm}$
 (c) $5 \times 10^{10} \text{ dpm}$ (d) $7.5 \times 10^{20} \text{ dpm}$

SOLUTION

1. (b): The hardness of the effluent sample is $\frac{6}{28}$ th of the hardness of the CaCl_2 solution.

Hardness of CaCl_2 solution = ?

111 parts of $\text{CaCl}_2 \equiv 100$ parts CaCO_3

$$0.136 \text{ parts (mol. wt.) of } \text{CaCl}_2 = \frac{100}{111} \times 0.136$$

$$= 0.123 \text{ parts of } \text{CaCO}_3$$

0.136 g of CaCl_2 in 1000 parts of $\text{H}_2\text{O} = 0.123$ in 10^6 parts = 123

Hardness of $\text{CaCl}_2 = 123 \text{ ppm}$

$$\text{Hardness of effluent sample} = \frac{6}{28} \times 123 = 26 \text{ ppm}$$

2. (c) 3. (c) 4. (b) 5. (b) 6. (b)

7. (a): The lines at the red end belong to Balmer series. These are obtained for jumps to $n = 2$ from outer orbits (1^{st} line from $n = 3$, 2^{nd} line from $n = 4$, 3^{rd} line from $n = 5$).

8. (c) 9. (a)

10. (c): $h\nu = h\nu_0 + KE$, $\nu - \nu_0 = \frac{KE}{h}$

Given, $(KE)_2 = 2(KE)_1$

$$\therefore \nu_2 - \nu_0 = 2(\nu_1 - \nu_0)$$

$$\text{or } 3.2 \times 10^{16} - \nu_0 = 2(2 \times 10^{16} - \nu_0)$$

$$\text{or } \nu_0 = 0.8 \times 10^{16} \text{ Hz} = 8 \times 10^{15} \text{ Hz}$$

11. (d): When intensity is doubled, number of electrons emitted per second is also doubled but average energy of photoelectrons emitted remains same.

12. (d): Radius of nucleus $= 1.25 \times 10^{-13} \times A^{1/3} \text{ cm}$
 $= 1.25 \times 10^{-13} \times 64^{1/3}$
 $= 1.25 \times 10^{-13} \times 4 \text{ cm}$
 $= 5 \times 10^{-13} \text{ cm}$

Radius of atom $= 1 \text{ \AA} = 10^{-8} \text{ cm}$

$$\frac{\text{Volume of nucleus}}{\text{Volume of atom}} = \frac{(4/3)\pi(5 \times 10^{-13})^3}{(4/3)\pi(10^{-8})^3}$$

$$= \frac{125 \times 10^{-39}}{10^{-24}} = 125 \times 10^{-15} = 1.25 \times 10^{-13}$$

13. (c) 14. (c) 15. (d) 16. (b) 17. (d)

18. (a): δ , charge = $\frac{\text{Dipole moment}}{d}$

$$= \frac{0.38 \times 10^{-18} \text{ esu-cm}}{1.61 \times 10^{-8}} = 2.4 \times 10^{-11} \text{ esu}$$

$$\% \text{ of charge} = \frac{2.4 \times 10^{-11} \text{ esu}}{4.8 \times 10^{-10} \text{ esu}} \times 100 = 5\%$$

19. (d): Total pressure = 1 atm

$$\therefore \text{partial pressure} = 1 - 0.3 = 0.7 \text{ atm}$$

When capacity is changed, vapour pressure does not change, only the partial pressure of

N_2 changes, so $p_{N_2} = \frac{0.7}{3} = 0.233 \text{ atm}$

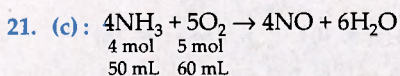
So, total pressure = $0.233 + 0.3 = 0.533 \text{ atm}$

$$20. (d) : \sqrt{\frac{8RT}{\pi M_A}} = \sqrt{\frac{3RT}{M_B}}$$

$$\frac{8}{\pi M_A} = \frac{3}{M_B}, \frac{M_A}{M_B} = \frac{8}{3\pi}$$

$$\text{for } \sqrt{\frac{8RT}{\pi M_A}} = \sqrt{\frac{3RT'}{\pi M_B}}, \frac{T}{M_A} = \frac{T'}{M_B};$$

$$\frac{3\pi T}{8M_B} = \frac{T'}{M_B}, \frac{T}{T'} = \frac{8}{3\pi}, \therefore T' > T$$



Equal mol contains equal volume under given conditions.

$\text{H}_2\text{O}_{(g)}$ obtained from 50 mL of NH_3 $\frac{6 \times 50}{4} = 75 \text{ mL}$

$\text{H}_2\text{O}_{(g)}$ obtained from 60 mL of O_2 $\frac{6 \times 60}{5} = 72 \text{ mL}$

Hence, O_2 is limiting reactant. Hence, 72 mL water vapour is produced.

$$22. (b) : P_1 V = n_1 RT, P_2 V = n_2 RT$$

$$\frac{n_2}{n_1} = \frac{P_2}{P_1}, n_2 = \frac{12}{120} \times \frac{0.01}{100} = 10^{-5}$$

1 mol contains 6.023×10^{23} molecules
 $\therefore 10^{-5} \text{ mol}$ contains 6.023×10^{18} molecules.

$$23. (d) \quad 24. (c)$$

$$25. (a) : G = H - TS$$

$$Y = c + mx \quad \therefore m = -S$$

$$26. (a) : \text{Mass} = \text{Volume} \times \text{density} = 20 \text{ g}$$

Change in temperature, $\Delta T = 7.6^\circ\text{C}$
 Heat evolved = $4.18 \times 20 \times 7.6 = 6.4 \times 10^2 \text{ J}$
 Moles of $\text{Ag}^+ = 10.0 \times \frac{1}{1000} = 10^{-2} \text{ mol}$
 Moles of $\text{AgCl} = 10^{-2} \text{ mol}$
 Heat evolved per mole of AgCl
 $= \frac{6.4 \times 10^2}{1 \times 10^{-2}} = 64 \text{ kJ/mol AgCl}$
 $\Delta H = -64 \text{ kJ}$

$$27. (b) \quad 28. (a)$$

$$29. (d) : \text{Molecular mass of } \text{NH}_4\text{NO}_3 = 80$$

Molar heat of decomposition (for bomb calorimeter) = $\frac{C \times \Delta T \times M}{m}$

$$\therefore \Delta H = \frac{1.23 \times 6.12 \times 80}{1} = 602 \text{ kJ}$$

As heat of decomposition is always negative.

$$\therefore -602 \text{ kJ}$$

30. (b): As coal has 80% carbon in weight
 weight of carbon in 10 kg coal

$$= 10 \times \frac{80}{100} = 8 \text{ kg} = 8000 \text{ g}$$

As 60% of C is converted to CO_2
 thus wt. of C converted into CO_2

$$= 8000 \times \frac{60}{100} = 4800 \text{ g}$$

and 40% of C to CO thus wt. of C converted into

$$\text{CO} = 8000 \times \frac{40}{100} = 3200 \text{ g}$$

Now from eq. (i) 12 g (1 mole) of C on combustion liberates = 394 kJ of heat

\therefore 4800 g of C on combustion liberates

$$= \frac{394 \times 4800}{12} \text{ kJ} = 157600 \text{ kJ} \quad \dots(i)$$

From eq. (ii) 12 g (1 mole) of C on combustion liberates = 111 kJ of heat

\therefore 3200 g of C on combustion liberates

$$= \frac{111 \times 3200}{12} \text{ kJ} = 29600 \text{ kJ}$$

Total heat liberated would be = $157600 + 29600 = 187200 \text{ kJ}$

31. (b): Ag^+ ions required to precipitate Cl^-

$$= \frac{K_{sp}(\text{AgCl})}{0.05}$$

Ag^+ ions are required to precipitate CrO_4^{2-}

$$= \left[\frac{K_{sp}(\text{Ag}_2\text{CrO}_4)}{0.05} \right]^{1/2}$$

$$32. (c) : \quad \begin{array}{cccc} P & + & Q & = & R & + & S \end{array}$$

$$\text{Initial moles} \quad a \quad a \quad 0 \quad 0$$

$$\text{At equilibrium} \quad a - x \quad a - x \quad x \quad x$$

$$\Rightarrow x = \frac{a}{3}$$

$$K_c = \frac{x^2}{(a-x)(a-x)}, \frac{a^2}{9 \times (2x)^2} = \frac{(3x)^2}{9 \times 4x^2}$$

$$K_c = \frac{1}{4} = 0.25, \text{ but } K_c = \frac{k_f}{k_b}$$

$$\text{or } k_b = \frac{k_f}{K_c} = \frac{2 \times 10^{-3}}{0.25} = 8 \times 10^{-3}$$

$$33. (d) : \text{Slope} = \tan \theta = \frac{\Delta H^\circ}{2.303R}$$

$$0.5 = \frac{\Delta H^\circ}{2.303 \times 8.314}$$

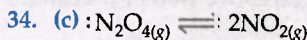
$$\Delta H^\circ = 9.574 \text{ J mol}^{-1}$$

$$\text{Intercept} = \log_{10} A = 10, A = 10^{10}$$

$$\log K = 10 - \frac{9.574}{2.303 \times 8.314 \times 298}$$

$$K = 9.96 \times 10^9$$

As ΔH° is independent of temperature, equilibrium constant remains almost constant. It means even at 798 K, equilibrium constant $K = 9.98 \times 10^9$

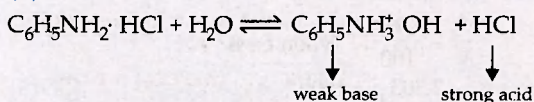


$$\text{Degree of dissociation } x = \frac{D-d}{d} \text{ or } x = \frac{D}{d} - 1$$

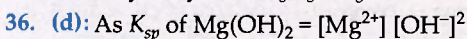
At Y, $x = 0$

$$\therefore \frac{D}{d} - 1 = 0 \text{ or } \frac{D}{d} = 1$$

35. (b):



Therefore the solution formed will be acidic, due to the hydrolysis of $\text{C}_6\text{H}_5\text{NH}_3^+$ ion.

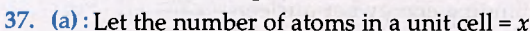


$$\therefore [\text{OH}^-]^2 = \frac{1.2 \times 10^{-11}}{0.1} = 1.2 \times 10^{-10}$$

$$\therefore [\text{OH}^-] = 1.1 \times 10^{-5}$$

$$[\text{H}^+] = 10^{-14} / 1.1 \times 10^{-5} = 0.91 \times 10^{-9}$$

$$\text{pH} = -\log [\text{H}^+] = \log 0.91 \times 10^{-9} = 9.04$$



$$\text{Mass of } x \text{ atoms i.e., one unit cell} = \frac{60 \times x}{6 \times 10^{23}}$$

$$\begin{aligned} \text{Volume of the unit cell} &= (\text{edge length})^3 \\ &= (400 \times 10^{-12} \times 100)^3 = (400 \times 10^{-10} \text{ cm})^3 \\ &= (4 \times 10^{-8} \text{ cm})^3 = 64 \times 10^{-24} \text{ cm}^3 \end{aligned}$$

$$\text{Density} = 6.25 = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$\therefore 6.25 = \frac{60 \times x}{6 \times 10^{23} \times 64 \times 10^{-24}}$$

$$x = \frac{6.25 \times 6 \times 64 \times 10^{-1}}{60} = 4$$

Since the unit cell contains 4 atoms, so it is face-centred cubic unit cell.

38. (c)

39. (a): In zinc blende structure, S^{2-} ions are arranged in ccp while Zn^{2+} ions occupy half of the tetrahedral sites.

40. (a)

$$41. (a): d = \frac{Z \times M}{N_A \times V} \text{ or } Z = \frac{d \times N_A \times V}{M}$$

$$a = 5 \text{ \AA} = 5 \times 10^{-8} \text{ cm}$$

$$\text{Molecular mass, } M = 56 + 16 = 72 \text{ g}$$

$$Z = \frac{4 \times 6.023 \times 10^{23} \times 125 \times 10^{-24}}{72} = 4.16 \approx 4$$

Four molecules of ferrous oxide, FeO per unit cell – it means 4Fe^{2+} and 4O^{2-} .

42. (c): For NaCl type structure,

$$\frac{r_+}{r_-} = 0.414 - 0.737$$

For maximum possible radius of A

$$\frac{r_+}{r_-} = 0.414; r_- = \frac{170}{0.414} = 410.6$$

$$43. (a): M_2(\text{obs}) = \frac{K_f \cdot w \cdot 1000}{W \cdot \Delta T_f}$$

$$= \frac{5.12 \times 2.0 \times 10^{-2} \times 1000}{1.0 \times 0.69} = 148.4$$

Calculated molecular mass of phenol = 94

$$i = \frac{M_2(\text{cal})}{M_2(\text{obs})} = \frac{94}{148.4} = 0.633$$



$$\text{Total species} = (1 - \alpha) + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}$$

$$i = \frac{1 - \alpha/2}{1} \text{ or } \frac{\alpha}{2} = 1 - i$$

$$\text{or } \alpha = 2(1 - i) = 2(1 - 0.633) = 0.734 = 73.4\%$$

44. (d): Solubility in water = 0.2/200 mL

Solubility in ether = 0.4/50 mL or 1.6/200 mL

$$\Rightarrow \frac{S_{\text{ether}}}{S_{\text{water}}} = \frac{1.6}{0.2} = 8$$

45. (a)

46. (c)

47. (c)

48. (a): Loss in weight or water bulb in which water vapour from solution flowed in and vapour from pure water escaped $\propto p^\circ - p$. Gain in weight of CaCl_2 tube being the weight of water vapour from pure water $\propto p^\circ$

$$\frac{\text{Loss in wt. of water bulb}}{\text{Gain in wt. of } \text{CaCl}_2 \text{ tube}} = \frac{p^\circ - p}{p^\circ} = \frac{0.087}{2.036} = \frac{n_2}{n_1}$$

$$\Rightarrow \frac{0.08}{2.036} = \frac{26.66 / M_2}{200 / 18} \Rightarrow M_2 = 56.16$$

49. (b)

50. (a): When the same amount of electricity is passed, then the masses of different ions liberated at the electrodes are directly proportional to their chemical equivalent.

$$\frac{W_1}{W_2} = \frac{E_1}{E_2} = \frac{z_1}{z_2} \Rightarrow \frac{108}{31.5} = \frac{x}{1.05}$$

$$\Rightarrow x = 3.6 \text{ g silver deposited}$$

$$51. (c): \alpha = \frac{\Lambda_{eq}^\circ}{\Lambda_{eq}^\circ} = \frac{10}{200} = 0.05$$

$$[H^+] = c\alpha = 1 \times 0.05 = 0.05$$

$$pH = -\log [H^+] = -\log (5 \times 10^{-2})$$

$$= 2 \log 10 - \log 5 = 2 - 0.6990 = 1.3.$$

52. (a): $\Lambda_m^\circ(\text{NH}_4\text{OH}) = \lambda_{\text{NH}_4^+}^\circ + \lambda_{\text{OH}^-}^\circ = 72 + 198$
 $= 270 \Omega^{-1} \text{cm}^2$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ} = \frac{9}{270} = \frac{1}{30} = 3.33\%$$

53. (b): $\text{Pt} | \text{H}_2(1 \text{ atm}) | \text{HA}_2 | | \text{HA}_1 | \text{H}_2(1 \text{ atm}) | \text{Pt}$
 At anode $E_{\text{H}/\text{H}^+} = E^\circ_{\text{H}/\text{H}^+} + 0.059 (\text{pH})_2$

$$(\because \text{pH} = -\log[H^+])$$

$$\text{At cathode } E_{\text{H}^+/\text{H}} = E^\circ_{\text{H}^+/\text{H}} - 0.059 (\text{pH})_1.$$

$$\text{We know, } [H^+] = C\alpha = \sqrt{K_a C}$$

$$\text{pH}_1 = \frac{1}{2} \text{p}K_{a1} - \frac{1}{2} \log C, \text{pH}_2 = \frac{1}{2} \text{p}K_{a2} - \frac{1}{2} \log C$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{H}/\text{H}^+} + E^\circ_{\text{H}^+/\text{H}}$$

$$\therefore 0.059 \left[\frac{1}{2} \text{p}K_{a2} - \frac{1}{2} \text{p}K_{a1} \right] = \frac{0.059}{2} (5 - 3) = 0.059 \text{ V}$$

54. (d): When equal volumes of A and B are mixed both the solutions get doubly diluted, hence individual contribution of $A = \frac{\kappa_1}{2}$ and that of $B = \frac{\kappa_2}{2}$.

Total specific conductance of the mixture

$$= \frac{1}{2} (\kappa_1 + \kappa_2) = \frac{1}{R} x$$

$$\text{Thus, } R = \frac{2x}{\kappa_1 + \kappa_2}$$

55. (b) 56. (d)

57. (c): Vessel III has highest concentration of reactants, $c = \frac{n}{v} = \frac{0.2}{0.1} = 2 \text{ mol/L}$ (for each reactant)

Higher the concentration of reactants higher is the rate of reaction.

58. (c): $[A]_{\text{left}} = [B]_{\text{formed}} = n \times [A]_{\text{decayed}}$

$$C_0 e^{-kt} = n \times C_0 (1 - e^{-kt}) \quad \therefore e^{-kt} = \frac{n}{n+1}$$

$$\therefore [B]_{\text{formed}} = n \times C_0 \times (1 - e^{-kt})$$

$$= n \times C_0 \times \left(1 - \frac{n}{n+1} \right) = \frac{n C_0}{n+1}$$

59. (c): $\log k = \log A - \frac{E_a}{2.303RT}$

$$\text{Slope} = \frac{-E_a}{2.303R} = \frac{1}{2.303} (\text{given})$$

$$E_a = -2.303 R \times \text{slope} = R = -2 \text{ cal}$$

60. (a): In 1st case, fraction of A reacted

$$= \frac{0.6}{0.8} = \frac{3}{4} = 0.75$$

$$\text{In 2nd case, fraction of A reacted} = \frac{0.675}{0.9} = \frac{3}{4}$$

$$= 0.75$$

For a first order reaction, time taken for the same fraction of reaction is independent of initial concentration.

61. (b) 62. (d)

63. (a): a and b are two Langmuir parameters. At very high pressure, the above isotherm acquires the limiting form.

$$\frac{x}{m} = \frac{a}{b} \text{ (at very high pressure)}$$

64. (b): As we know lesser is gold number, more is the protective power of lyophilic colloid.

65. (c): $r_0 = 1600 = \ln N_0$

$$\frac{N_0}{N} = \frac{1600}{100}, \text{ when } t = 8$$

$$\delta = \frac{2.303}{\lambda} \log \frac{1600}{100}$$

$$\text{or } \lambda = 0.3466; \text{ now } r_0 = 1600; r_6 = ?; t = 6$$

$$6 = \frac{2.303}{\lambda} \log \frac{1600}{r_6} \quad \therefore r_6 = 200$$

66. (b): He atom has $2p + 2n$. Hence
 $\Delta m = (2 \times 1.0078 + 2 \times 1.0087) - 4.0026$
 $= 0.0304 \text{ amu}$

$$\therefore \text{Energy released} = 0.0304 \times 931.5 = 28.3 \text{ MeV}$$

$$\text{Binding energy per nucleon} = \frac{28.3}{4}$$

$$= 7 \text{ MeV (approximately)}$$

67. (b): Increase of Z by 1 with no change in m means emission of one β -particle. Decrease in Z by 2 and m by 4 means emission of one α -particle. No change in Z and m means emission of γ -rays.

68. (d): $N_0 = 1 \text{ gram atom} = 6.023 \times 10^{23} \text{ atoms}$
 Atoms disintegrated = 4.52×10^{23}

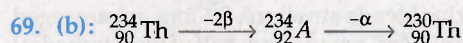
$$\text{Atoms left} = 6.023 \times 10^{23} - 4.52 \times 10^{23}$$

$$= 1.5 \times 10^{23}$$

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{10} \text{ hr}^{-1}$$

$$\therefore t = \frac{2.303 \times 10}{0.693} \log \frac{6.023 \times 10^{23}}{1.5 \times 10^{23}}$$

$$= 33.23 \log 4 = 20.1 \text{ hr}$$



70. (a): $\lambda = 2.5 \times 10^{-7} \text{ min}^{-1}$

$$\text{Mass of K-40} = 2.0 \text{ g}$$

$$N = \frac{2.0}{40} \times 6.02 \times 10^{23} = 3.01 \times 10^{22}$$

$$\text{Rate of decay} = \lambda N = 2.5 \times 10^{-7} \times 3.01 \times 10^{22}$$

$$= 7.5 \times 10^{15} \text{ dpm}$$

